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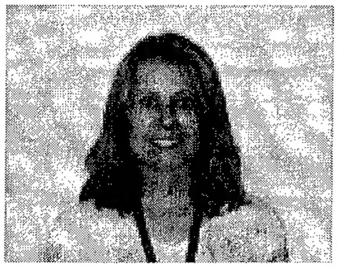
Design, Synthesis and Characterization of New Ionic Liquids

Greg Drake and Tom Hawkins
AFRL/PRSP
Air Force Research Laboratory
Edwards AFB, CA 93524

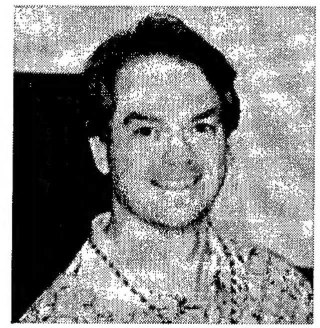
Ionic Liquids

Those involved in this work

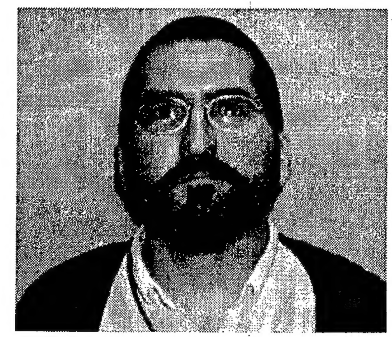


Ms. Kerri Tollison
Synthesis and
Characterization

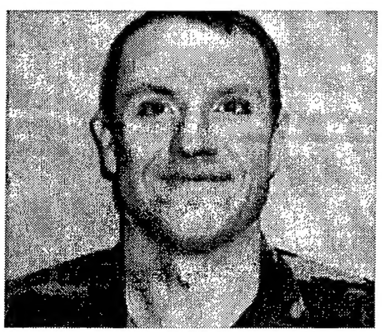
Greg Kaplan
Synthesis and
Characterization



Jerry Boatz
Theoretical
Calculations

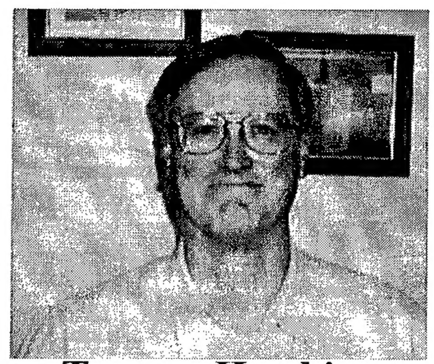


Jeff Mills
Theoretical
Calculations



Leslie Hall
Synthesis &
x-ray work

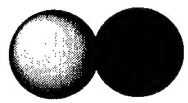
Ashwani Vij
X-ray
crystallography



Tommy Hawkins
6.2 Propellant
Development

Greg Drake
6.1 Research
Synthesis

Ionic Liquids



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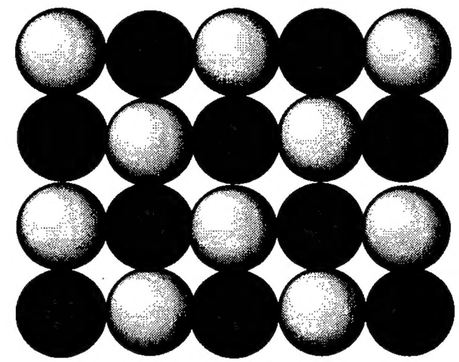
versus



Extended lattice

Table salt Na^+Cl^- m.p. = 804 °C Very high

Cryolite Na_3AlF_6 m.p. nearly 1000 °C (Hall Process for Al production)

Eutectic of Li^+Cl^- and K^+Cl^- m.p. 355 °C

<u>Molten salts are very hot</u>!

Not commercially viable

Corrosion and energy issues

Giant lattice of miniature magnets stuck together

Ionic Liquids

What are Ionic Liquids?
A class of salts consisting of cation/anion pair that has a very low melting point.

Definition of an ionic liquid is open to some debate amongst researchers in the area, but most in the area use one of two.

(1) An ionic compound that melts below 100 ^{o}C (b.p. of H_2O). J. Wilkes, P. Wasserscheid, K. Seddon.

(2) An ionic compound that has a melting point at or below ambient temperatures. These are often called RTILs (Room Temperature Ionic Liquids) T. Welton, R. Rogers.

But many of the salts fit both definitions and (2) is really a more specific class of (1).

Ionic Liquids

Important factors affecting the physical properties of ionic liquids

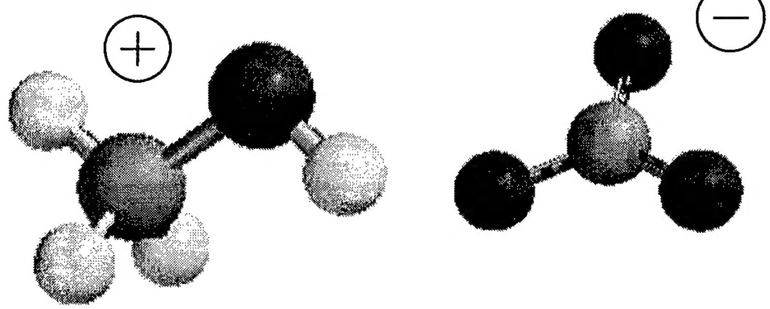
1. Asymmetry of cation as well as anion

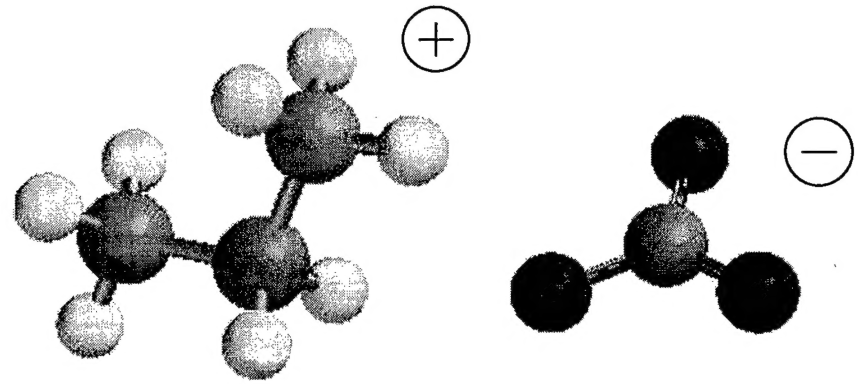
2. Packing efficiency

3. Charge delocalization in cationic/anionic species

4. "Sheer size" differentials

Ionic Liquids



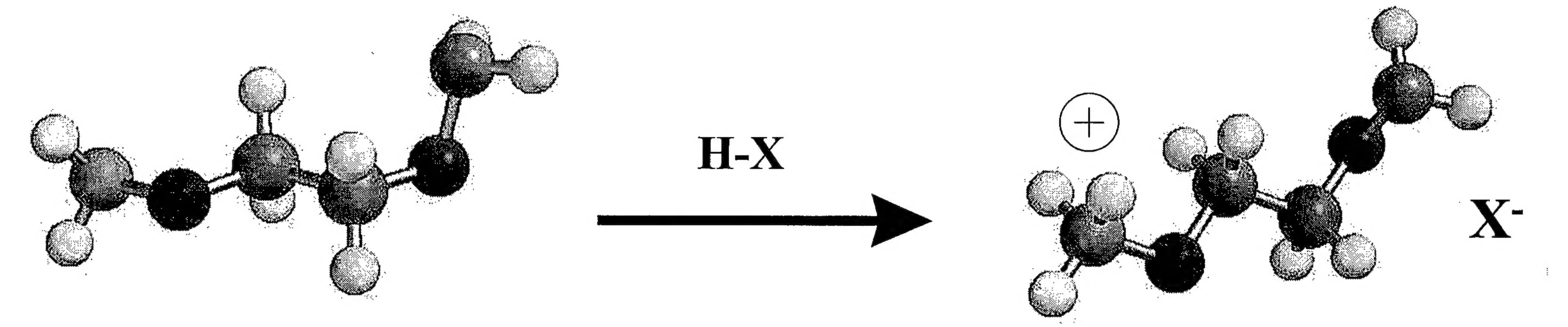


<u>Hydroxylammonium nitrate (HAN)</u>
$[NH_3OH^+][NO_3^-]$m.p. 39-40 °C

<u>Ethylammonium nitrate</u>
$[CH_3CH_2NH_3^+][NO_3^-]$ m.p. 12 °C

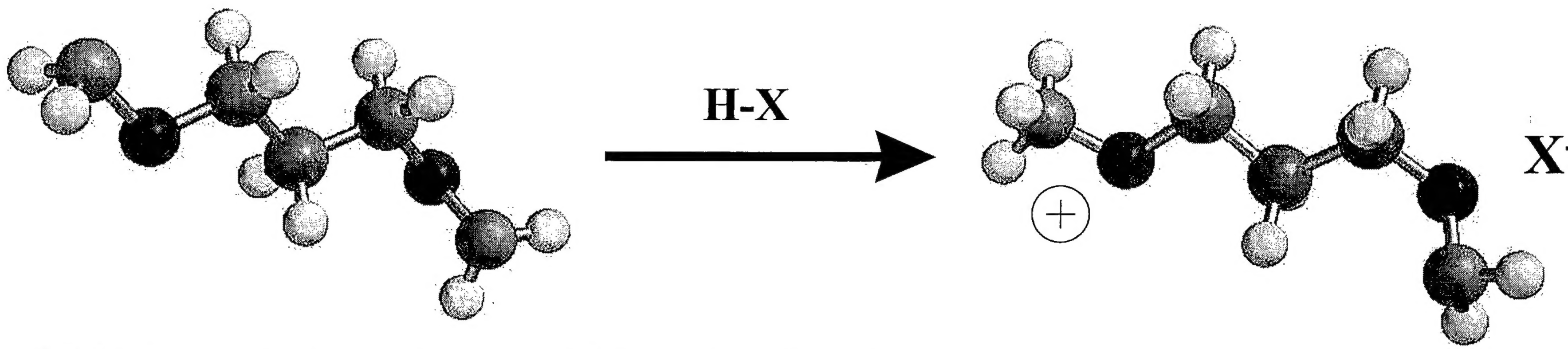
Serious issues...
- can be treacherous
- acidic
-very hygroscropic

Ionic Liquids



1,2-bis(oxyamine)ethane
Dixon, D. W. ; Weiss, R. H. J. Org. Chem. 1984, 49, 4487

1,2-bis(oxyamine)ethane mono salts
$X^- = NO_3^-$, ClO_4^- , $C(NO_2)_3^-$, $N(NO_2)_2^-$

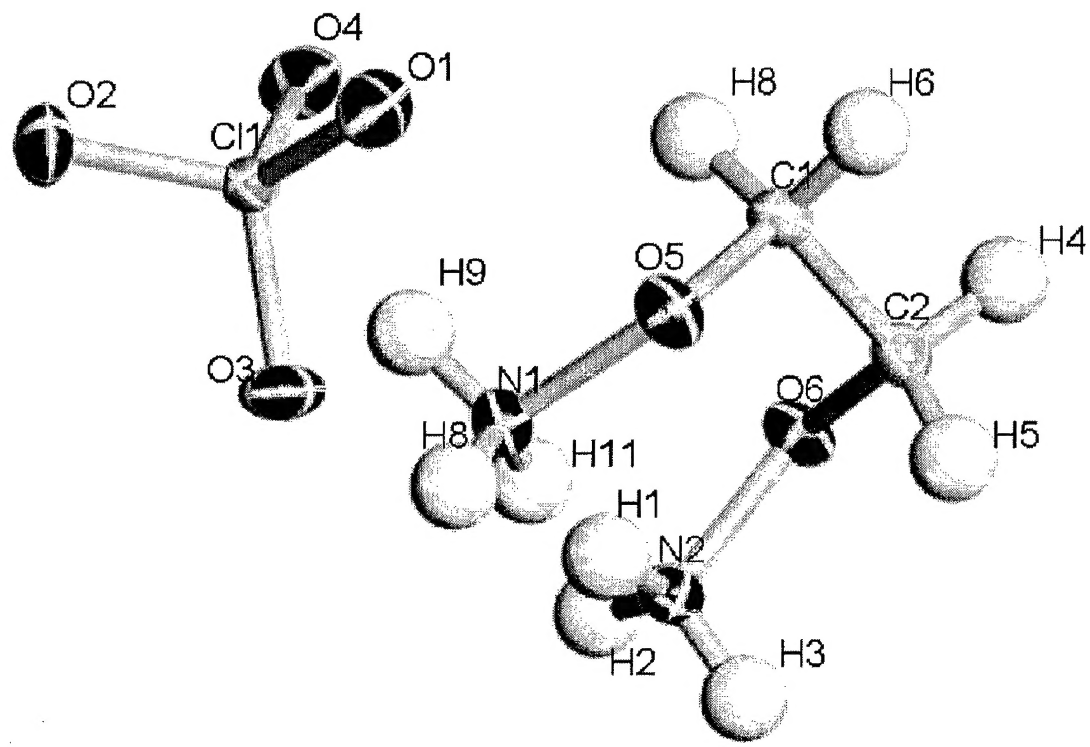


1,3-bis(oxyamine)propane very stable, watery liquid
b.p. = 65-70 C @ 0.3 torr; f.p. = glasses at -40 C

1,3-bis(oxyamine)propane mono salts
$X^- = NO_3^-$, ClO_4^- , $C(NO_2)_3^-$, $N(NO_2)_2^-$

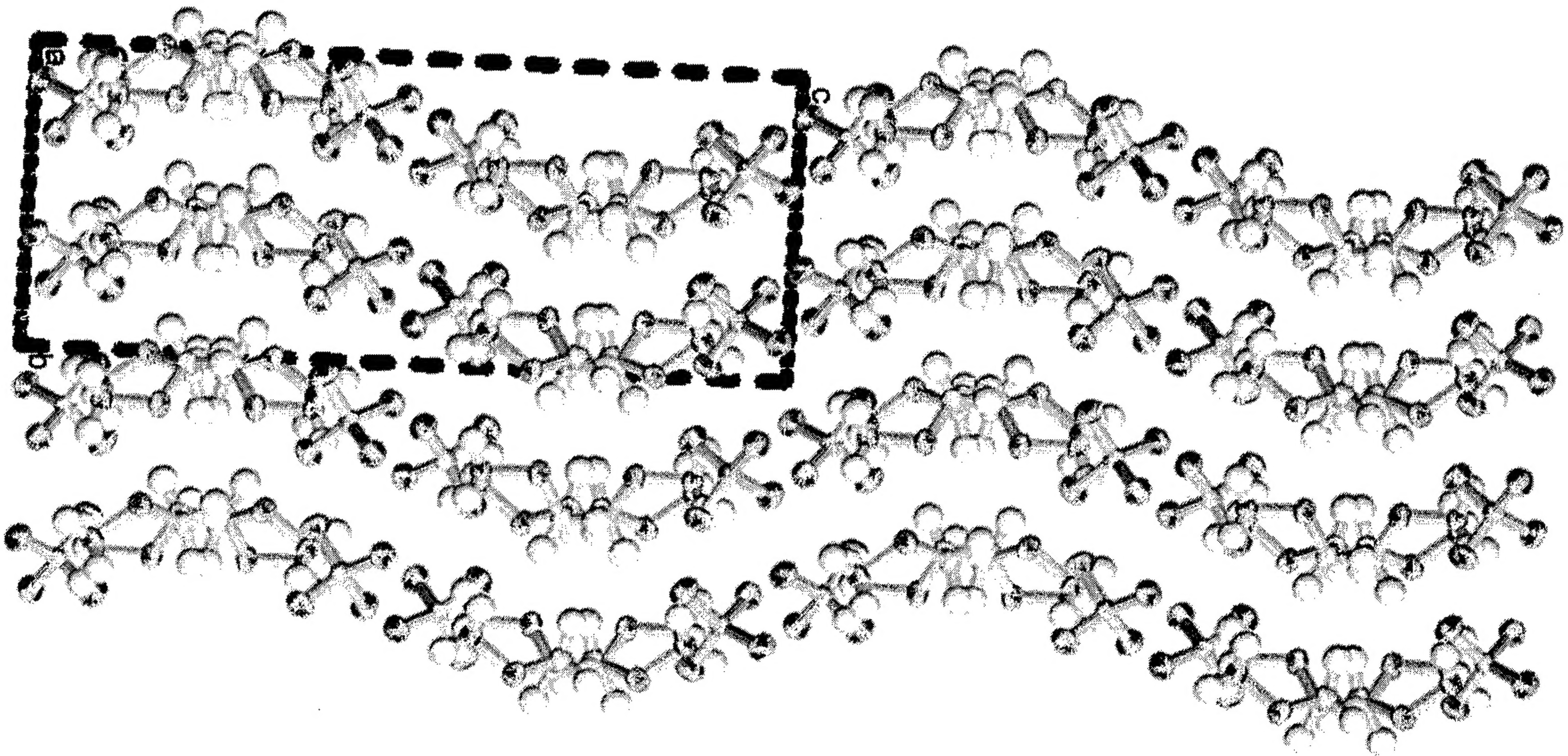
Bisoxyamines are stable as neutrals but protonated versions are not (extremely friction and impact sensitive!) Direct contrast with simple mono oxyamines.

Ionic Liquids



Single crystal x-ray structure of ethylene bisoxyamine monoperchlorate. Material has unusual amount of hydrogen bonding present ($\rho = 1.83$ g/cm^3!!!), but that doesn't explain its extreme sensitivity to impact and friction.

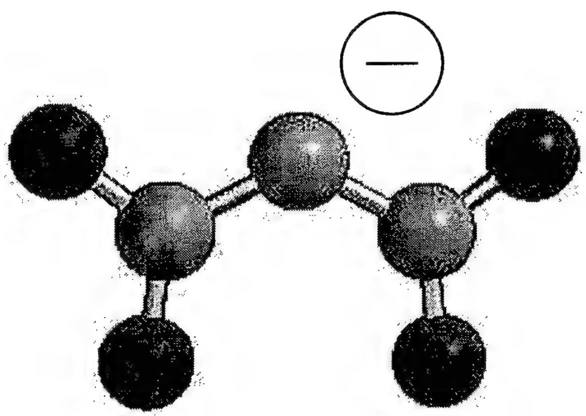
Ionic Liquids



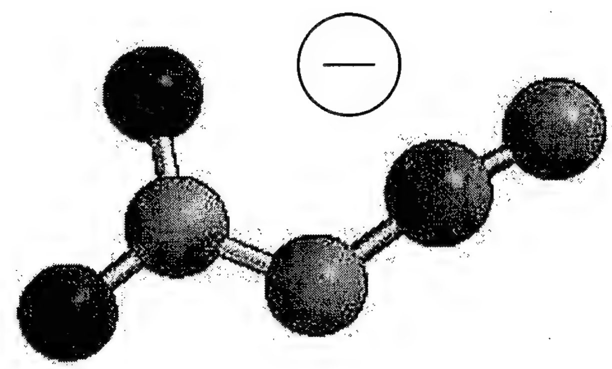
Extended lattice of ethylene bisoxyamine monoperchlorate.

Ionic Liquids

Since its western discovery in the late 1980's, by Jeff Bottaro, the dinitramide anion, $N(NO_2)_2^-$ has received tremendous attention as a potential new oxidizing anion for energetic materials. A closely related anion, the nitrocyanamide anion, $N(NO_2)(CN)^-$, was discovered in the early 1950's by McKay, and shortly thereafter, Harris investigated many heavy metal salts, as possible replacement initiators. However, it has been virtually ignored since that time.



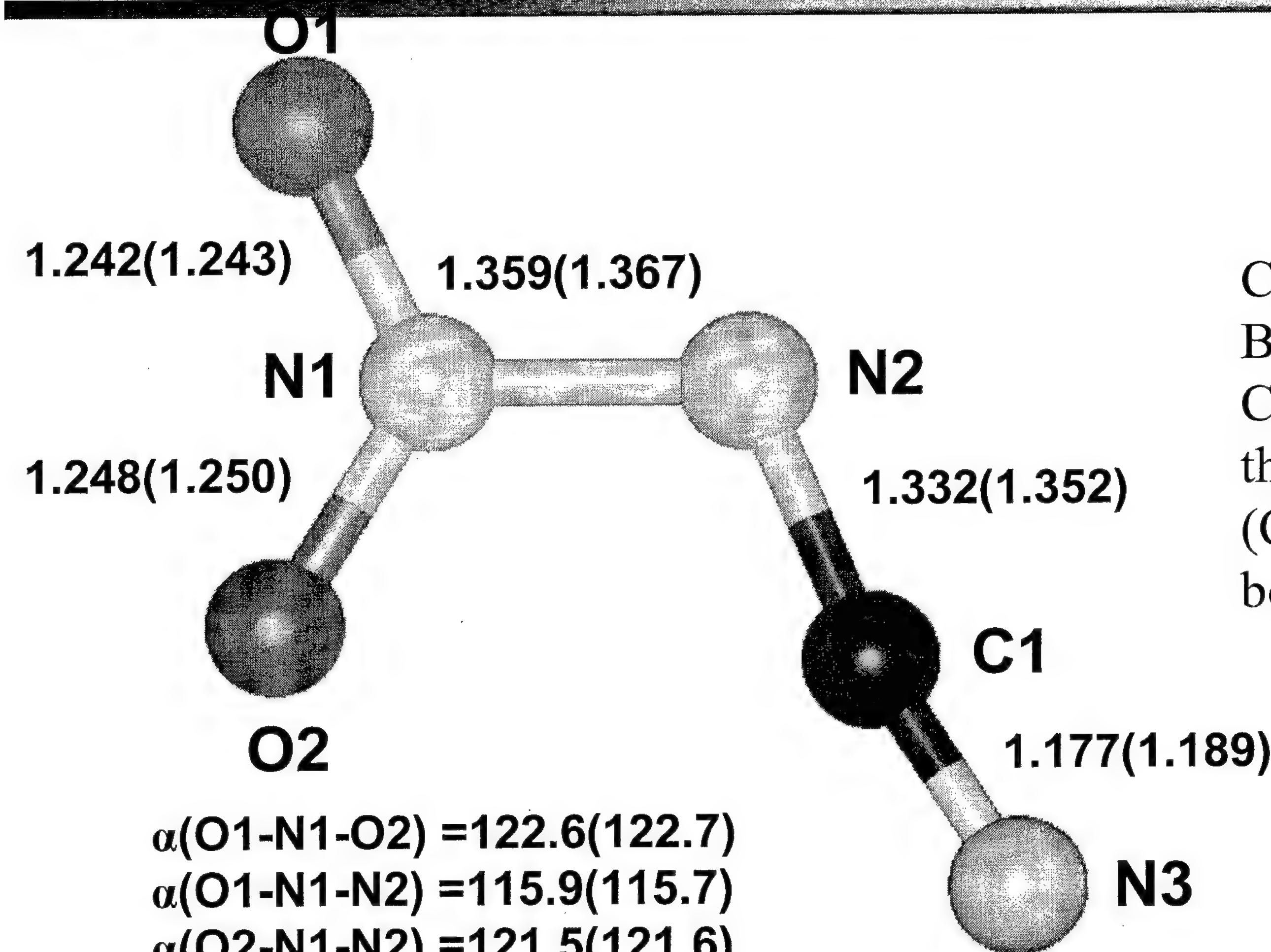
$N(NO_2)_2^-$ (dinitramide)



$N(NO_2)(CN)^-$ (nitrocyanamide)

Bottaro, J. L. ; Penwell, P. E. ; Schmitt, R. J. Synth. Commun., **1991**, *21*, 945.
McKay, A. F. ; Ott, W. L. ; Taylor, G. W. ; Buchanan, M. N. ; Crooker, J. F. Can. J. Chem. **1951**, *28*, 683. ; Harris, S. J. Amer. Chem. Soc. **1958**, *80*, 2302.

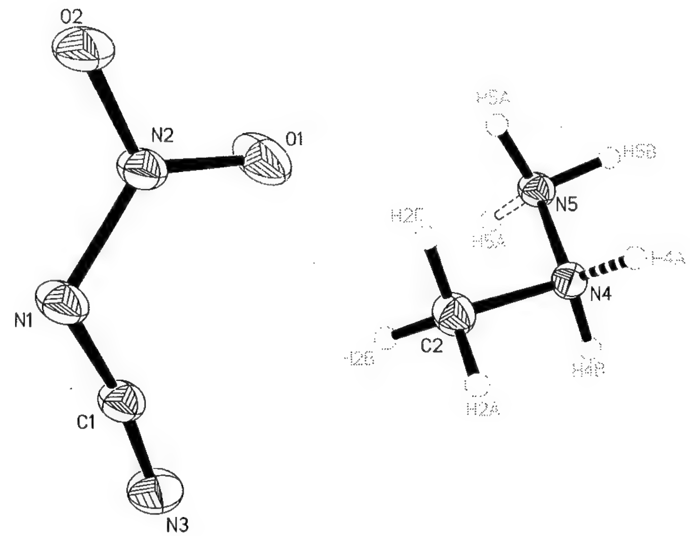
Ionic Liquids



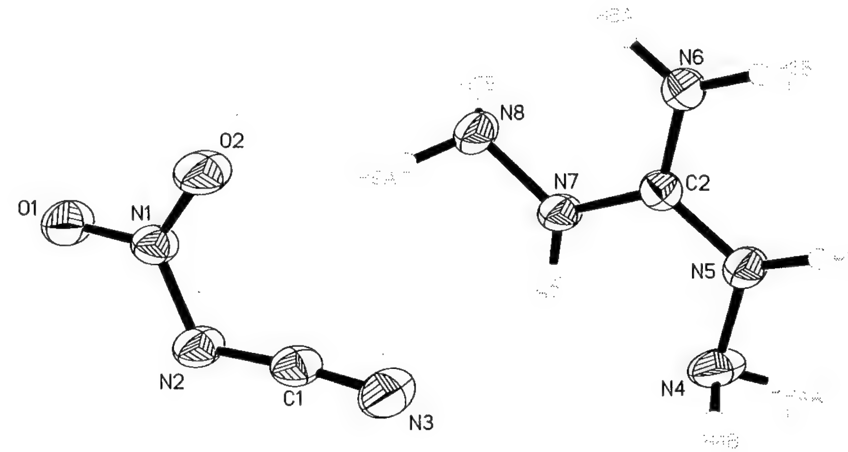
α(O1-N1-O2) =122.6(122.7)
α(O1-N1-N2) =115.9(115.7)
α(O2-N1-N2) =121.5(121.6)
α(N1-N2-C1) =113.7(111.3)
α(N2-C1-N3) =171.0(171.2)

Calculations using B3YLP/cc-pvdz and CCSD(T)/cc-pvdz levels of theory reveal a planar anion (C_s symmetry) with expected bond distances and angles.

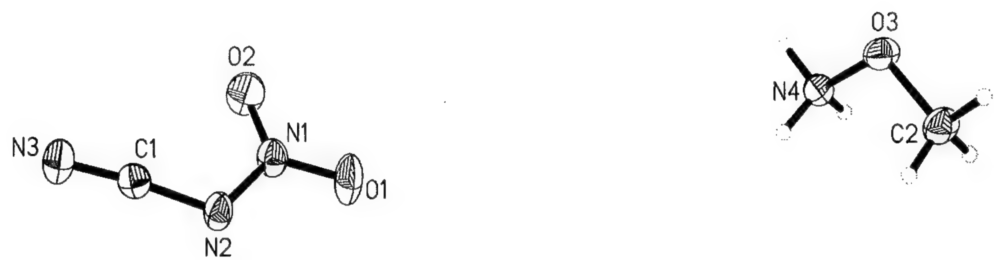
Ionic Liquids



Monomethylhydrazinium nitrocyanamide



Diaminoguanidinium nitrocyanamide



Methoxyammonium nitrocyanamide

Ionic Liquids

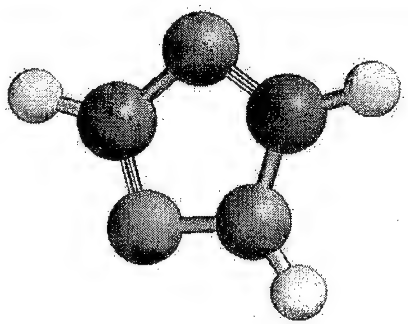
- **The syntheses of several nitrocyanamide salts were accomplished through the metathesis reactions of the appropriate halide salt with silver nitrocyanamide as Harris reported in 1958.**

$$[Ag^+][N(NO_2)(CN)^-] + [Cation^+][X^-] \text{ ---------}\rightarrow [Ag^+][X^-] + [Cation^+][N(NO_2)(CN)^-]$$

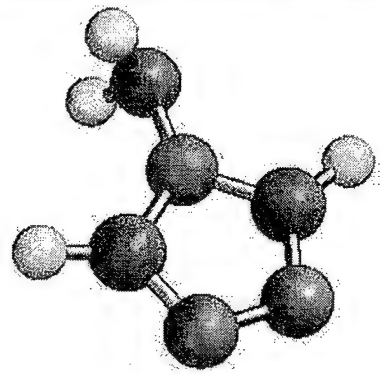
Compound	**ΔH_f(est) Kcal/mole**	**M.P. °C**	**Density g/cm^3 (meas.)**	**Impact kg-cm (5neg.)**	**Friction (Newtons) (5 neg.)**	**TGA % Loss/Day @ 75° C**
Hydrazinium nitrocyanamide	+14	109	1.53	10	76	> 1
Guanidinium nitrocyanamide	-13	95	1.39	>200	141	0.68
Methoxyammonium nitrocyanamide	-5	99	1.51	18	149	> 20
Monomethylhydrazinium nitrocyanamide	+4	57	1.44	>200	>371	1.9
Aminoguanidinium nitrocyanamide	0	94	1.50	>200	>371	0.9
Diaminoguanidinium nitrocyanamide	+10	108	1.52	>200	>371	1.6

$[NH_3OH^+]$ and $[HO\text{-}CH_2CH_2\text{-}NH_3^+]$ salts were made, but were not stable at ambient temperatures!

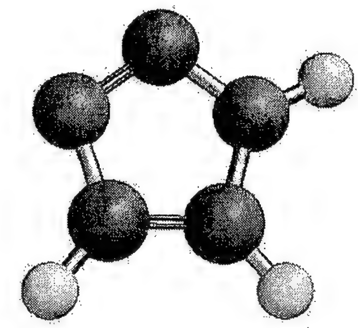
Ionic Liquids



1-H-1,2,4-triazole

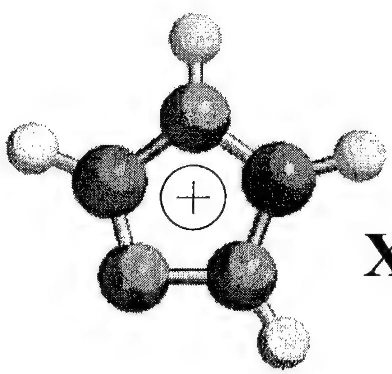


4-amino-1,2,4-triazole

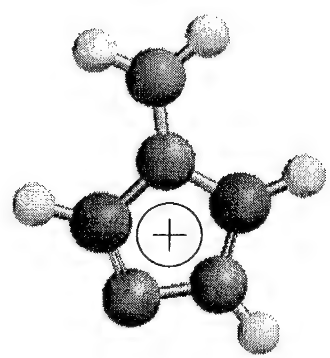


1-H-1,2,3-triazole

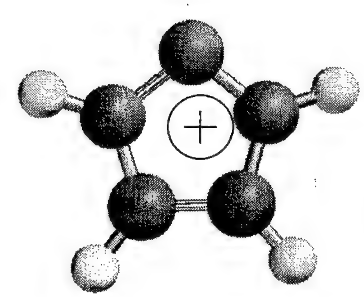
+H-X



X^-



X^-

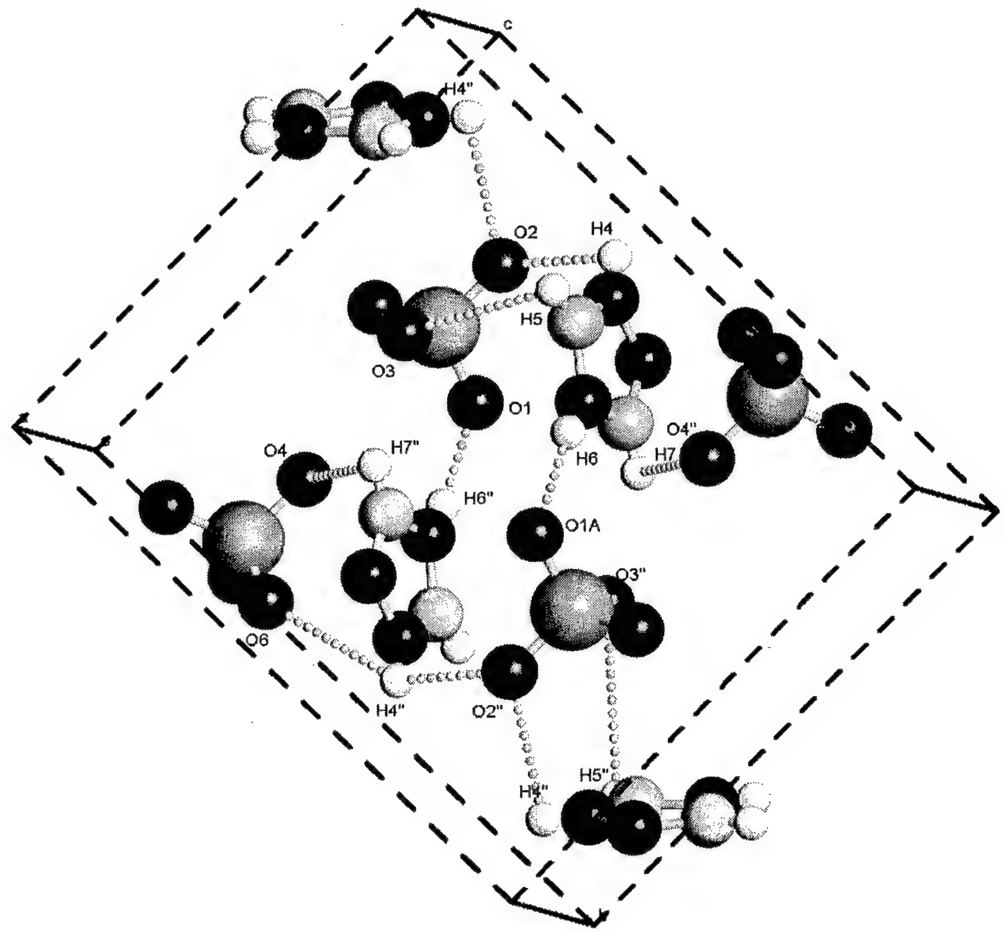


X^-

$X^- = NO_3^-, ClO_4^-, N(NO_2)_2^-$

Drake, G.W. ; Hawkins, T. ; Brand, A. ; McKay, M. ; Ismail, I. ; Hall, L. ;Vij, A. Prop. Explos. Pyrotech. **2003**, *12*, 1.

Ionic Liquids

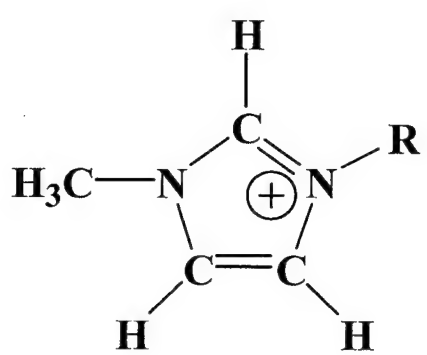


X-ray single crystal diffraction study of 1,2,4-triazolium perchlorate $\rho = 1.96$ g/cm^3
It is felt that this is probably the top of the hill density wise for simple heterocycle salts.

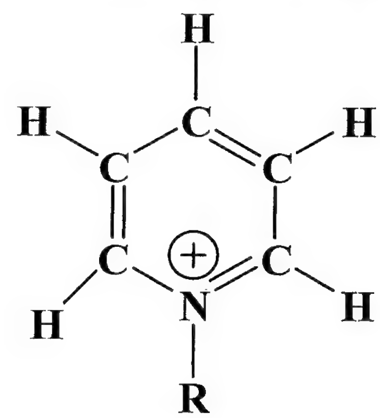
Drake, G.W. ; Hawkins, T. ; Brand, A. ; McKay, M. ; Ismail, I. ; Hall, L. ;Vij, A. Prop. Explos. Pyrotech. **2003**, *12*, 1.

Ionic Liquids

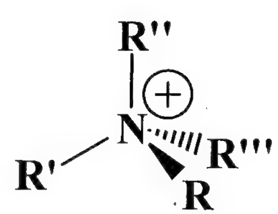
Some major shapes for organic based cations



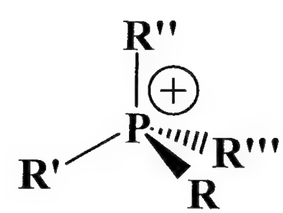
1-methyl-3-alkyl-imidazolium



1-alkylpyridinium



Tetraalkylammonium



Tetraalkylphosphonium

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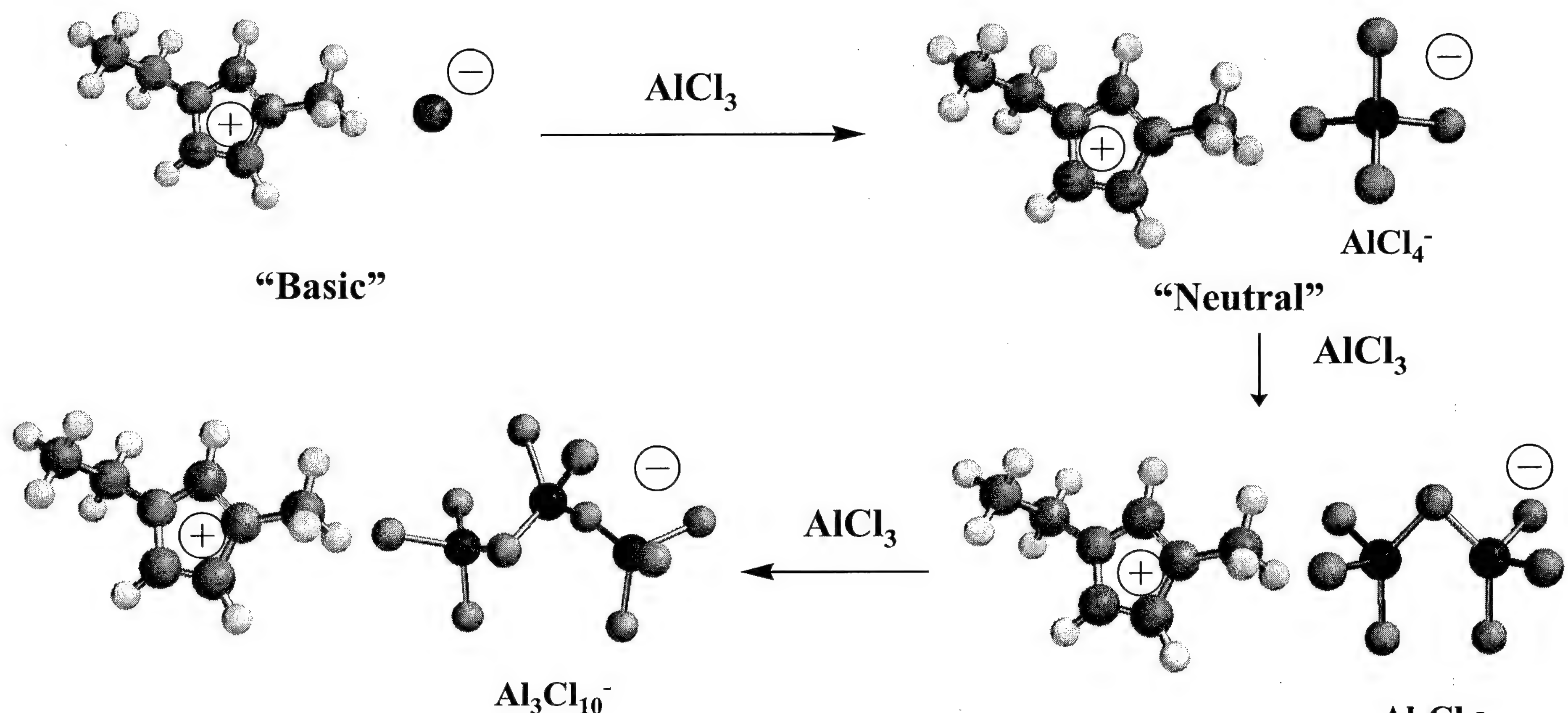
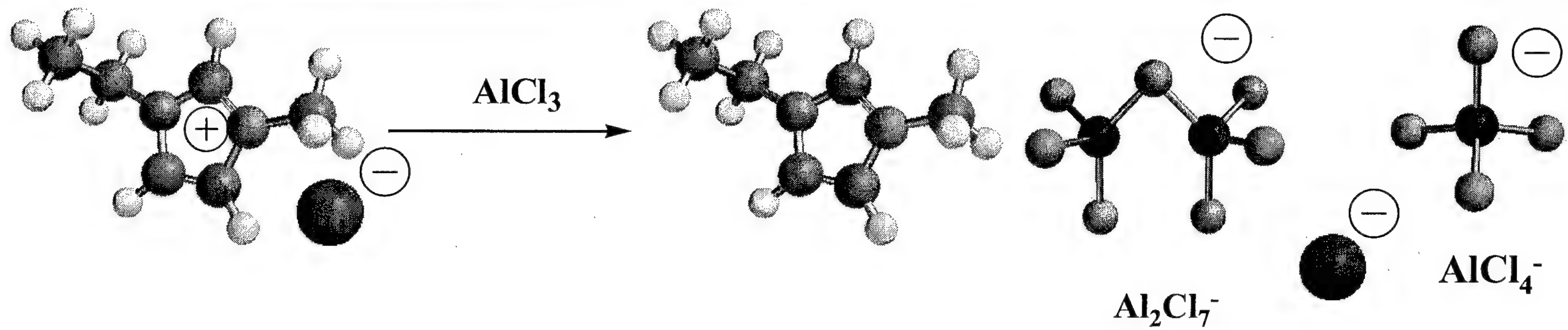
Ionic Liquids

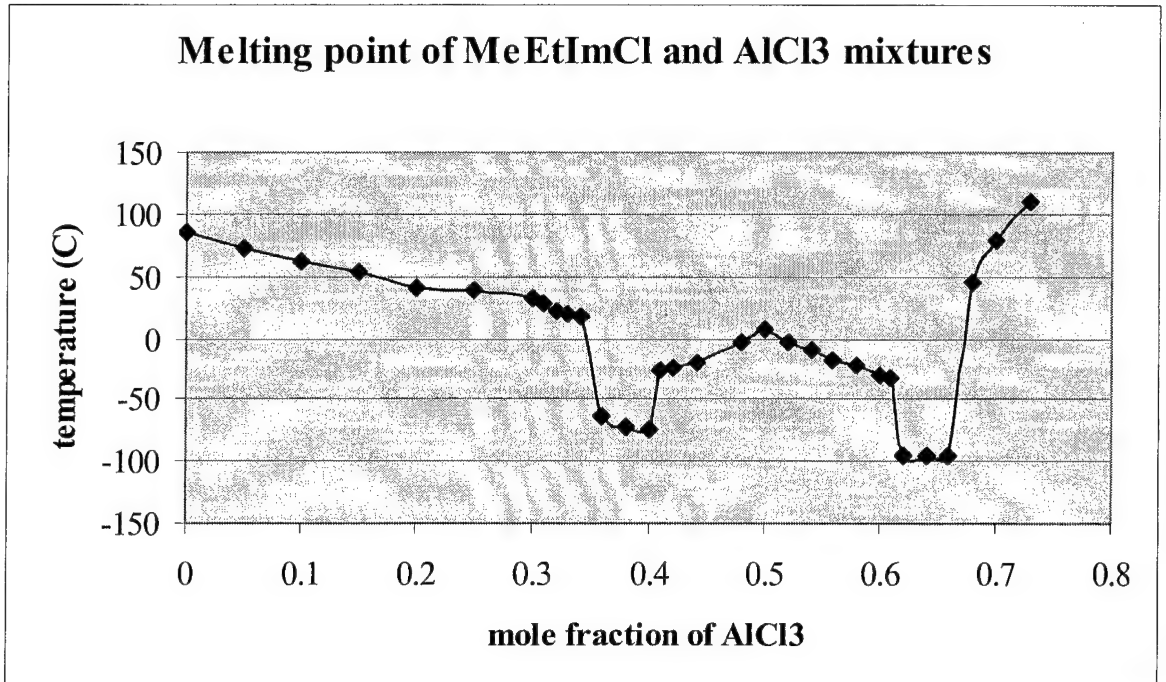
Significant efforts spent on 1-ethyl-3-methyl-imidazolium based systems and aluminum trichloride systems. More complex than originally thought as $AlCl_3$ and Cl^- have an equilibrium based on their respective concentrations.



Wilkes, J. S. Green Chemistry **2002**, *4*, 3.

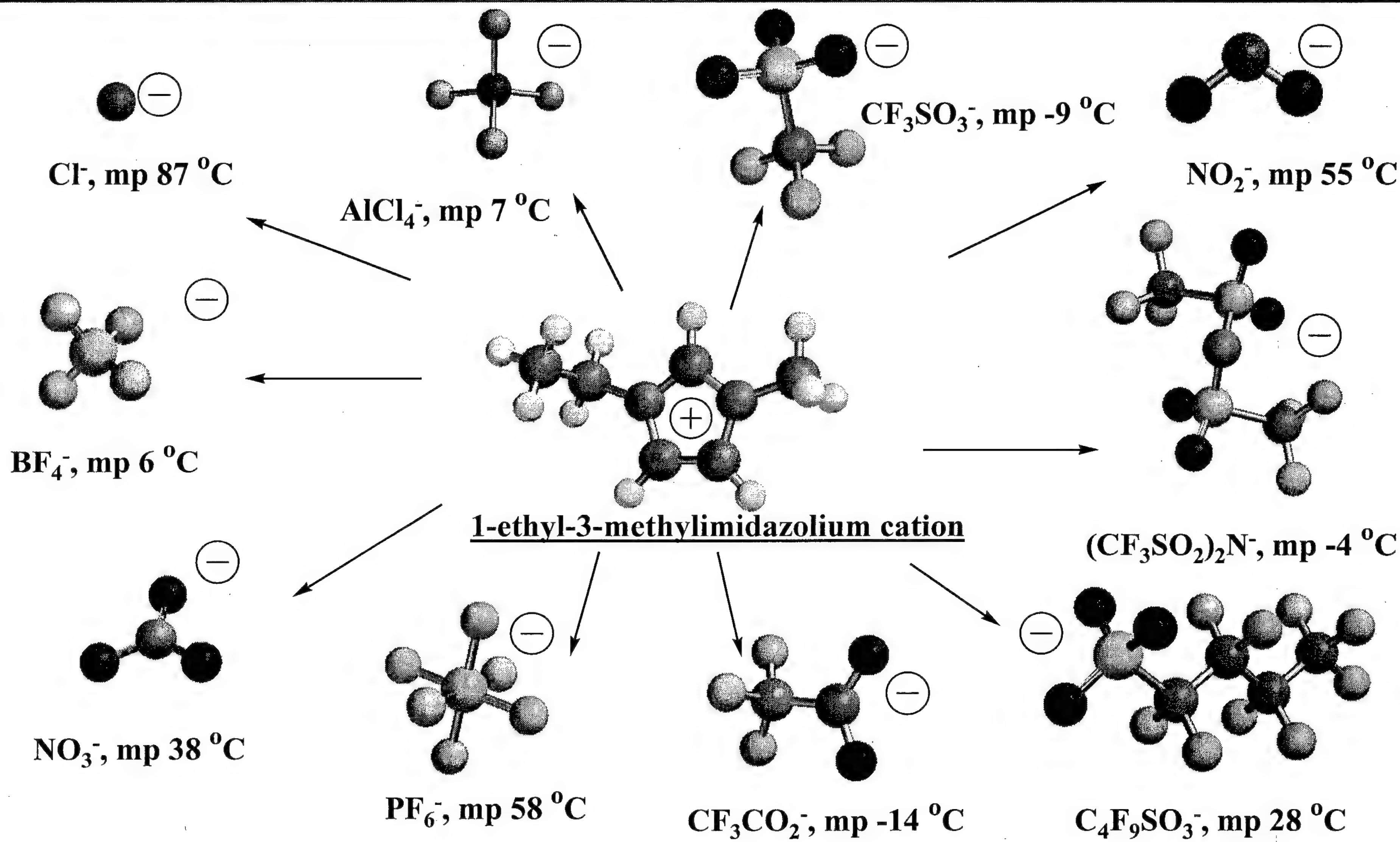
Ionic Liquids





Fannin, A. ; Floreani, D. ; King, L. ; Landers, J. ; Piersma, B. ; Stetch, D. ; Vaughn, R. ; Wilkes, J. ; Williams, J. J. Phys. Chem. **1984**, 88, 2614.

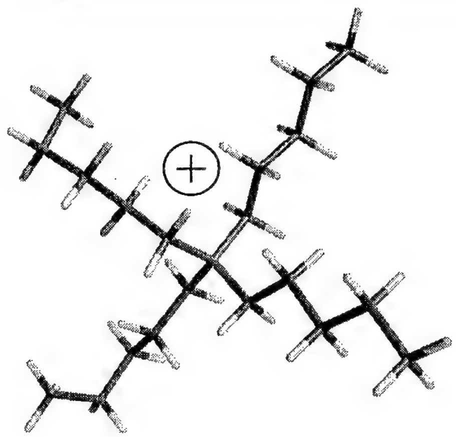
Ionic Liquids



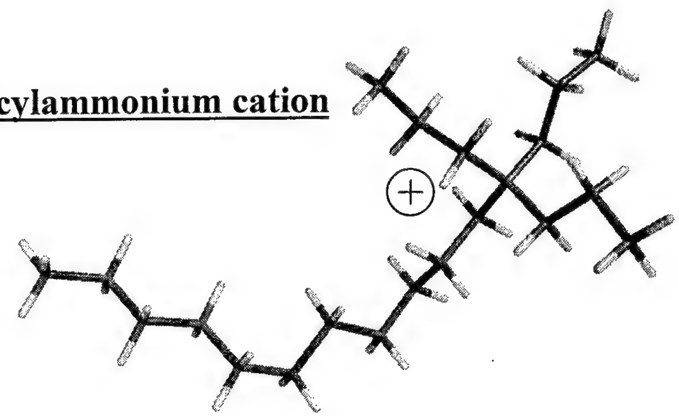
Wasserscheid, P.; Keim, W. Angew. Chem. Int. Ed. Engl. **2000**, 39, 3772. Wasserscheid, P, Welton, T. (eds.) Ionic Liquids in Synthesis Wiley-VCH, FRG, **2003** .Seddon, K.R. ; Holbrey, J. D. Clean Products and Processes **1999**, 1, 223. Rogers, R.; Seddon, K. (eds.) Ionic Liquids A.C.S. Symp. Ser. 818 2002 A.C.S Publ. Co.

Ionic Liquids

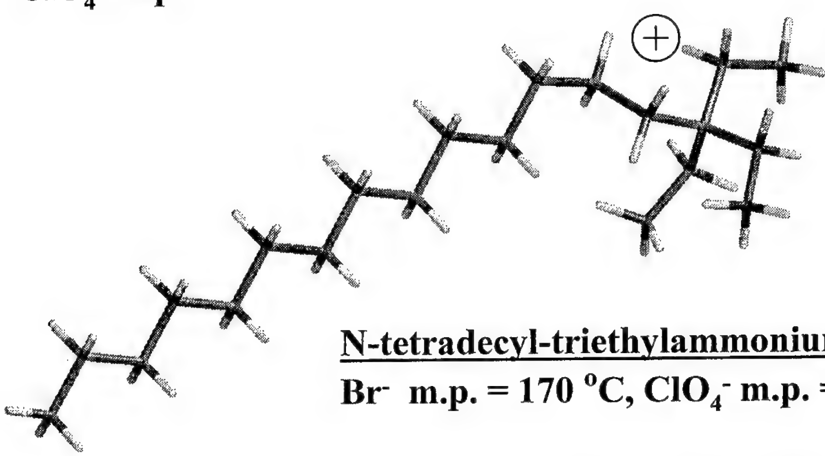
Substituted ammonium salts $R_4N^+X^-$ Variations in melting point based on cation structure.



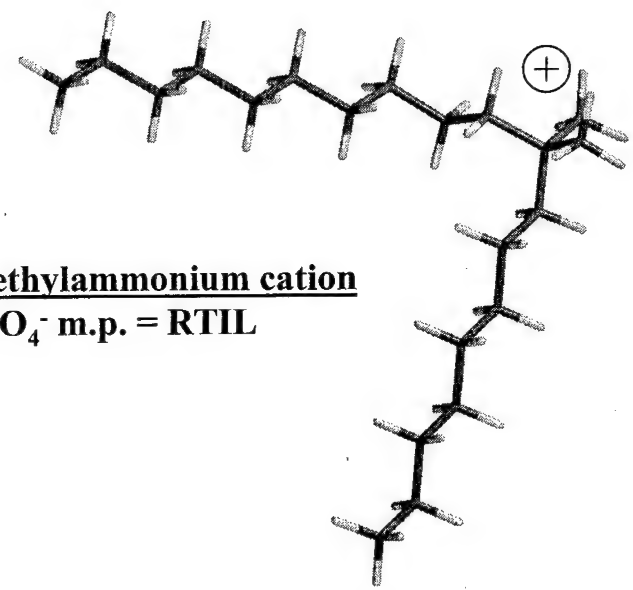
Tetra-n-pentylammonium cation
Br^- m.p. = 101 °C
ClO_4^- m.p. = 118 °C



Tris-(n-propyl)-undecylammonium cation
Br^- m.p. = 67 °C
ClO_4^- m.p. = 65 °C



N-tetradecyl-triethylammonium cation
Br^- m.p. = 170 °C, ClO_4^- m.p. = 152 °C



N-decyl-n-octyl-dimethylammonium cation
Br^- m.p. = RTIL, ClO_4^- m.p. = RTIL

Gordon, J. E. ; SubbaRao, G. N. J. Amer. Chem. Soc. **1978**, *100*, 7445.

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Ionic Liquids

Substituted ammonium salts $[R_4N^+][X^-]$Recently work has been done by using more desirable anions.

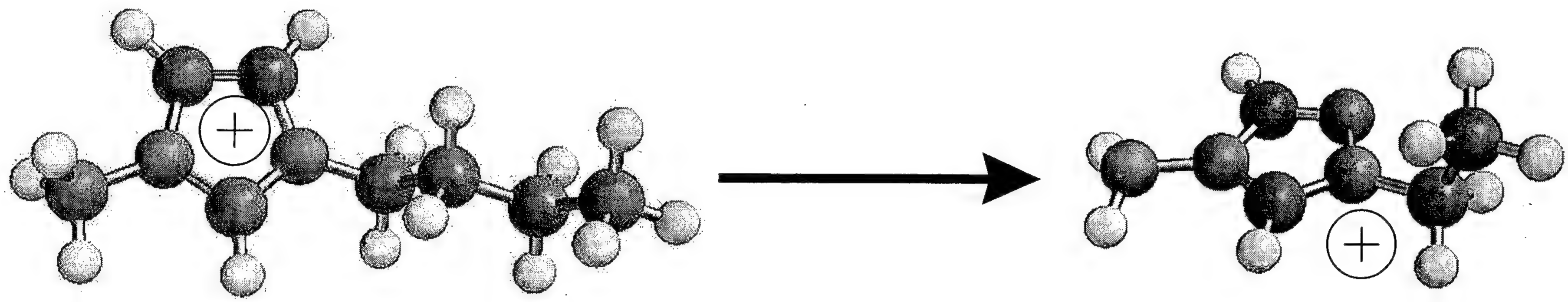
Substituted Ammonium Salt	M.P. (° C)	Density (g/cm³)	Viscosity (cp)	Λ (Ω^{-1} cm²/mole)
$[(n\text{-}C_6H_{13})(CH_3)_3N^+][N(SO_2CF_3)_2^-]$	-74 (g)	1.33	153	1.4
$[(n\text{-}C_7H_{15})(CH_3)_3N^+][N(SO_2CF_3)_2^-]$	-73 (g)	1.28	153	1.4
$[(n\text{-}C_8H_{17})(CH_3)_3N^+][N(SO_2CF_3)_2^-]$	-73(g)	1.27	181	1.3
$[(n\text{-}C_6H_{13})(CH_3CH_2)_3N^+][N(SO_2CF_3)_2^-]$	20	1.27	167	2.5
$[(n\text{-}C_7H_{15})(CH_3CH_2)_3N^+][N(SO_2CF_3)_2^-]$	-79	1.26	75	1.9
$[(n\text{-}C_8H_{17})(CH_3CH_2)_3N^+][N(SO_2CF_3)_2^-]$	-74	1.25	202	1.3
$[(n\text{-}C_6H_{13})(n\text{-}C_4H_9)_3N^+][N(SO_2CF_3)_2^-]$	26	1.15	595	0.8
$[(n\text{-}C_7H_{15})(n\text{-}C_4H_9)_3N^+][N(SO_2CF_3)_2^-]$	-67	1.17	606	0.8
$[(n\text{-}C_8H_{17})(n\text{-}C_4H_9)_3N^+][N(SO_2CF_3)_2^-]$	-63	1.12	574	0.7
$[(n\text{-}C_7H_{15})(Et)_3(ipr)_2N^+][N(SO_2CF_3)_2^-]$	-82	1.27	362	1.2
$[(n\text{-}C_8H_{17})(n\text{-}C_4H_9)_3N^+][OSO_2CF_3^-]$	-57	1.02	2030	0.07

-most have very low glass points
-densities decrease as expected
-viscosity increases dramatically with increasing alkyl length
-conductivity decreases with cation size (mobility issue)

Sun, J. ; Forsyth, M. ; MacFarlane, D. R. J. Phys. Chem. B **1998**, *102*, 8858.

Ionic Liquids

Most ionic liquids are based upon imidazolium rings and "heavy" or "dead" anions. We felt that we could use the shape of the cation and the poor fit idea to make much more energetic salts in a simple manner.

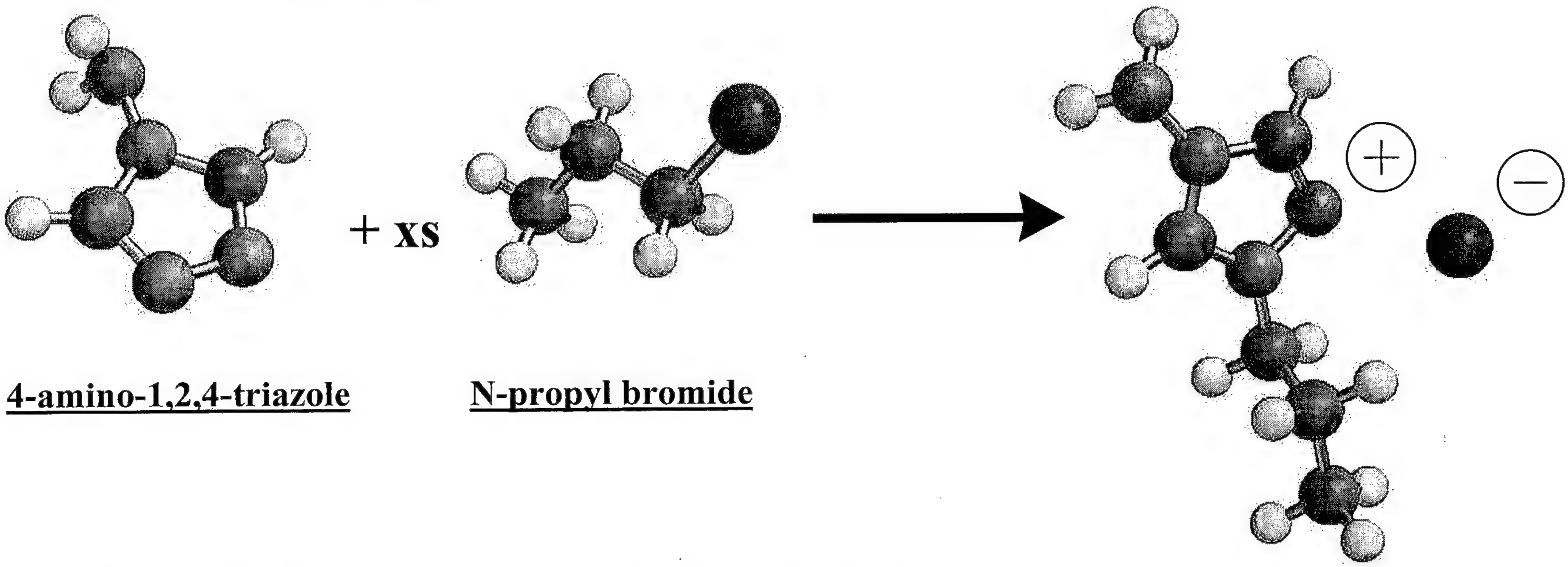


1-n-butyl-3-methyl imidazolium cation

1-ethyl-4-amino-1,2,4-triazolium cation

These new ionic liquids have similar shapes and physical properties, BUT higher ΔH_f, higher densities, and better oxygen balances.

Ionic Liquids



4-amino-1,2,4-triazole

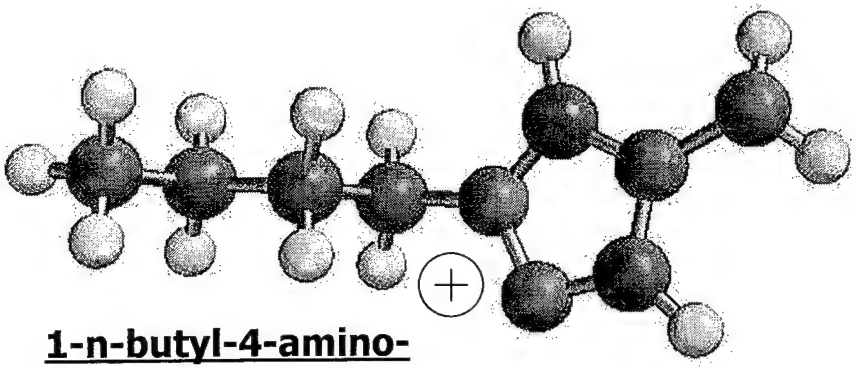
N-propyl bromide

1-n-propyl-4-amino-1,2,4-triazolium bromide
(yield >95% very pure)

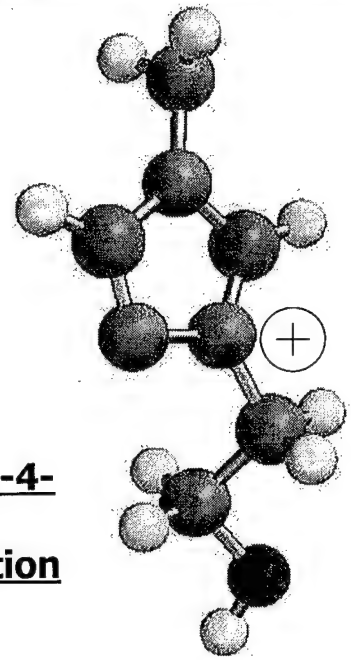
Synthesis is from commercial materials
High yield simple isolation has been known in literature for quite some time.

Scriven; Keay; Goe; Astleford J. Org. Chem. **1989**, *54*, 731.

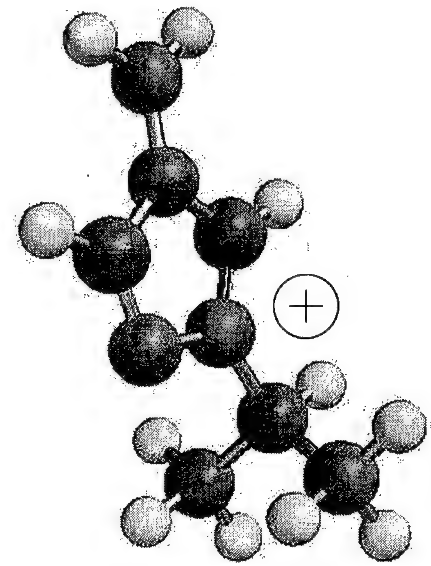
Ionic Liquids



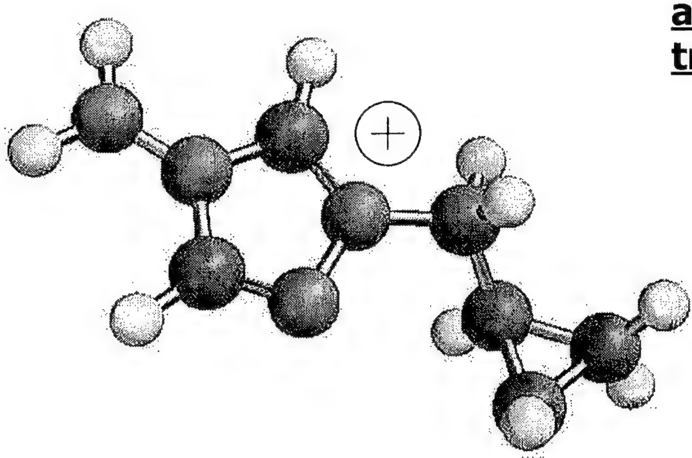
1-n-butyl-4-amino-1,2,4-triazolium cation



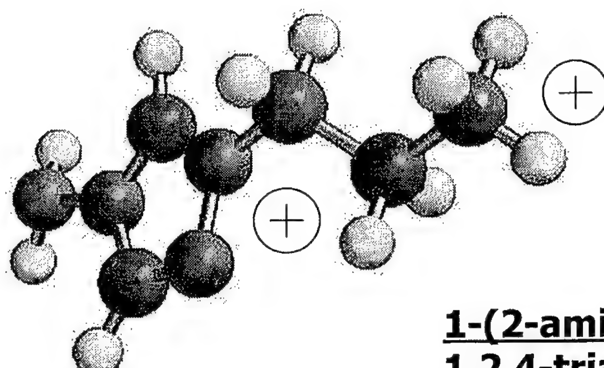
1-(2-ethanol)-4-amino-1,2,4-triazolium cation



1-isopropyl-4-amino-1,2,4-triazolium cation

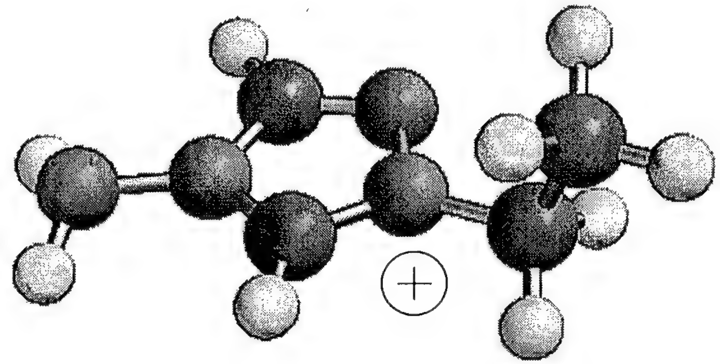


1-methylcyclopropyl-4-amino-1,2,4-triazolium cation

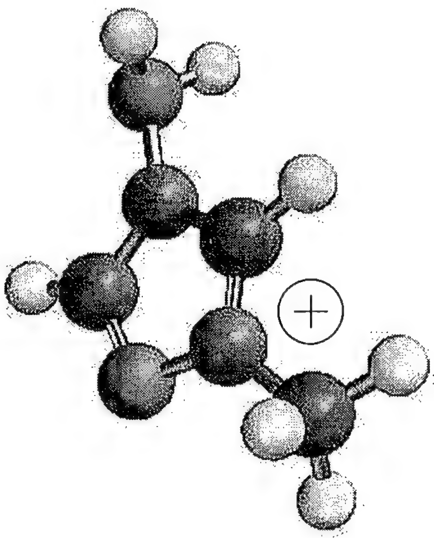


1-(2-aminoethyl)-4-amino-1,2,4-triazolium dication

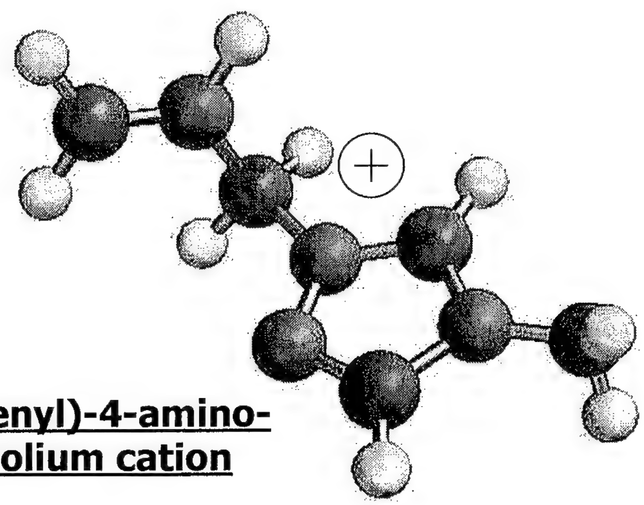
Ionic Liquids



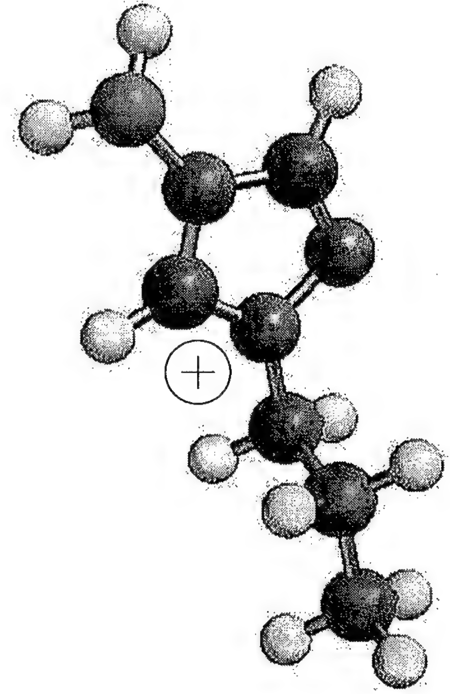
1-ethyl-4-amino-
1,2,4-triazolium cation



1-methyl-4-amino-
1,2,4-triazolium cation



1-(2-propenyl)-4-amino-
1,2,4-triazolium cation



1-n-propyl-4-amino-
1,2,4-triazolium cation

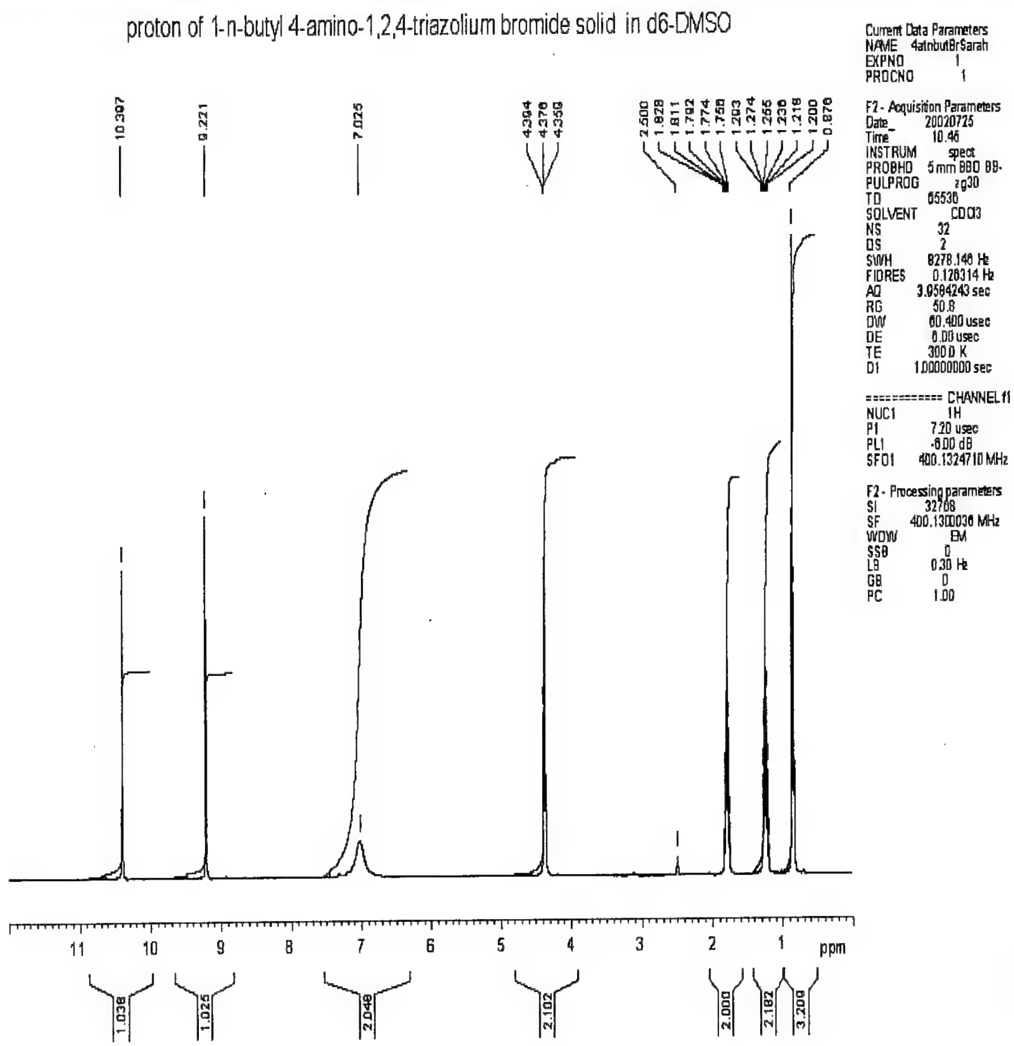
Ionic Liquids

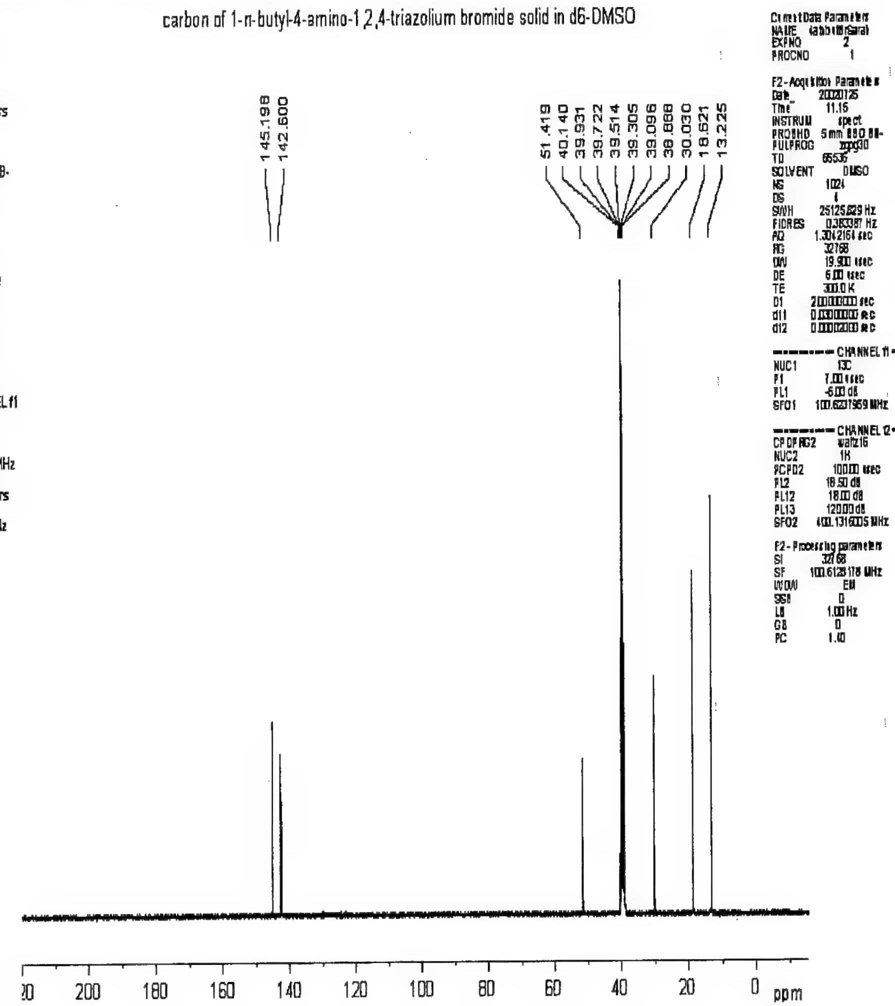
Physical properties of 1-n-alkyl substituted-4-amino-1,2,4-triazolium bromides.

- increasing melting points with increasing molecular weights,
- decomposition onsets that are relatively low
- densities decrease with increasing alkyl chain length.

Substituted 4AT salts	m.p. (°C)	dec. onset (°C)	density (g/cm^3)
1-ethyl	63°	110	1.69
1-n-propyl	60°	120	1.56
1-isopropyl	90°	110	1.60
1-butyl	48°	130	1.46
1-n-pentyl	54°	130	1.37
1-n-hexyl	76°	120	1.34
1-n-heptyl	94°	120	1.30
1-n-octyl	80°	135	1.27
1-n-nonyl	81°	140	1.26
1-n-decyl	90°	135	1.23

Ionic Liquids





^{1}H(left) and ^{13}C nmr spectra of 1-butyl-4-amino-1,2,4-triazolium bromide.

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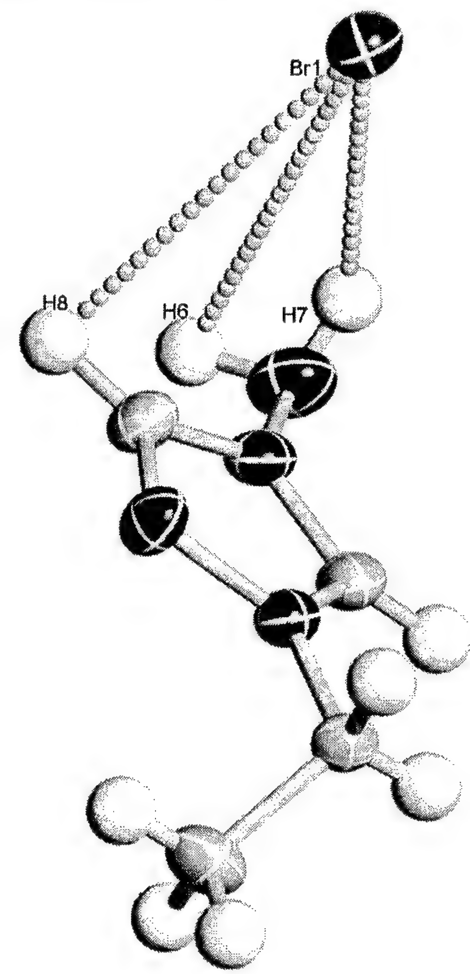
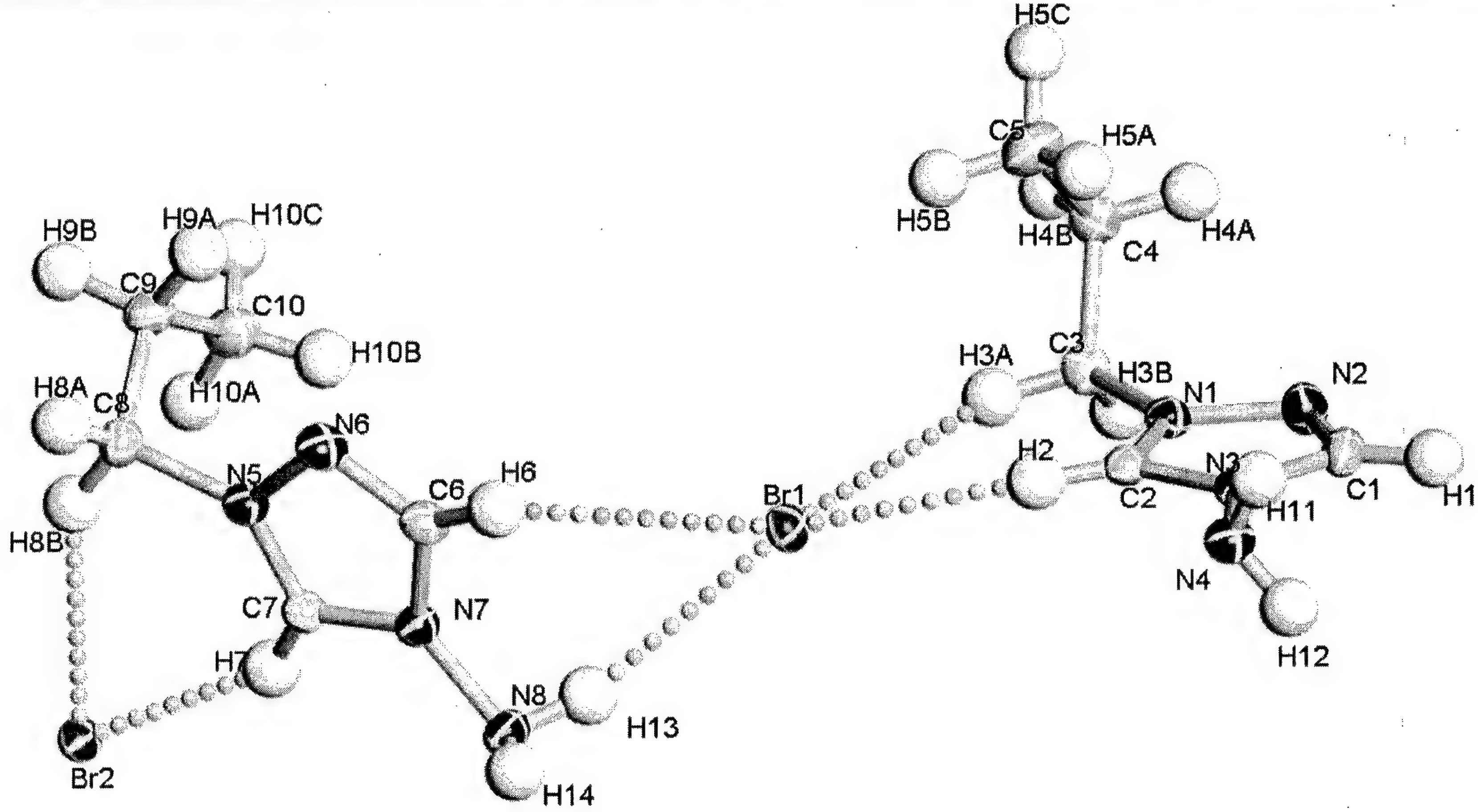
Ionic Liquids



Single x-ray diffraction study of 1-ethyl-4-amino-1,2,4-triazolium bromide.

Ionic Liquids



Single crystal x-ray diffraction study of 1-n-propyl-4-amino-1,2,4-triazolium bromide showing significant hydrogen bond contacts.

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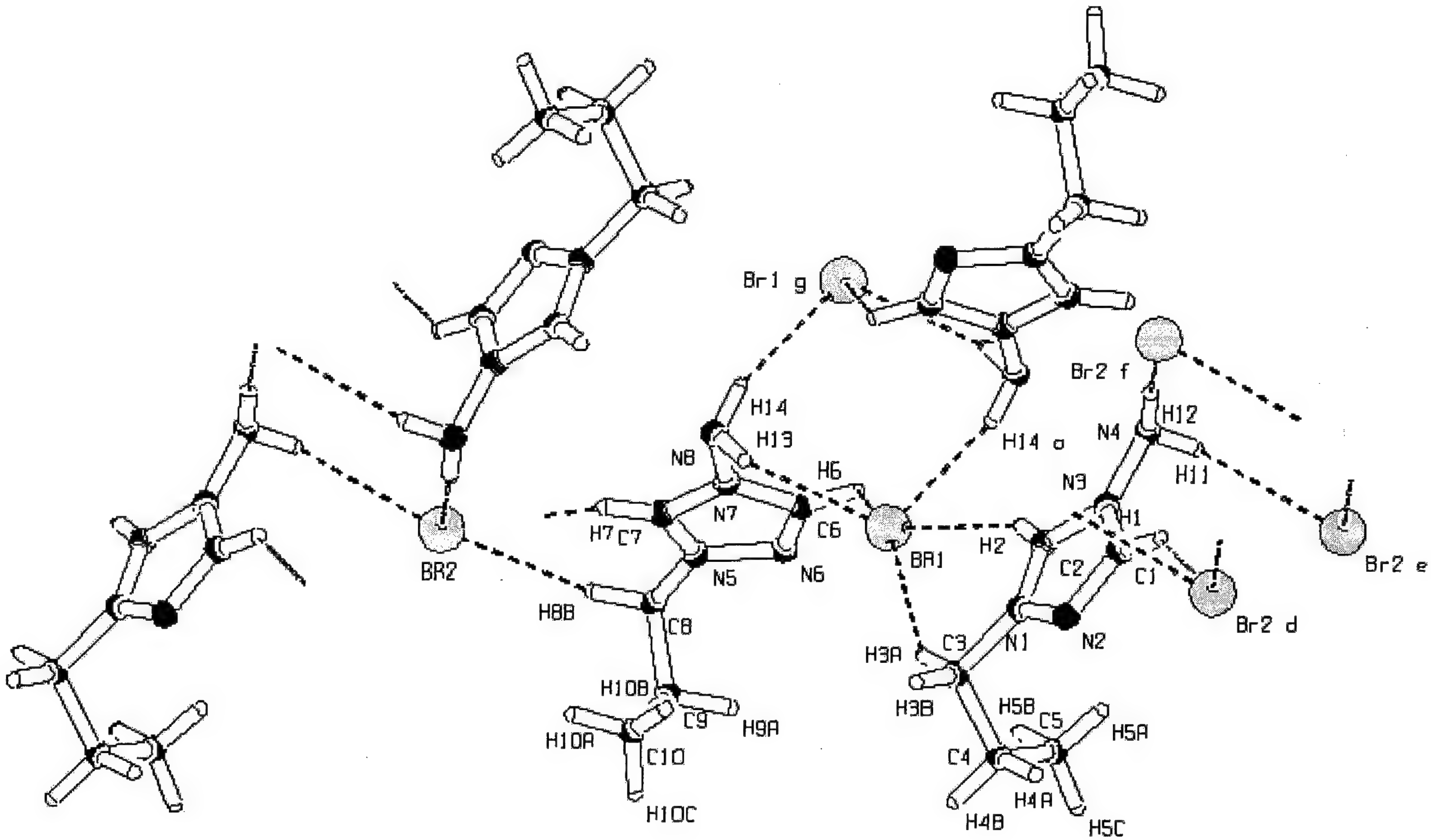
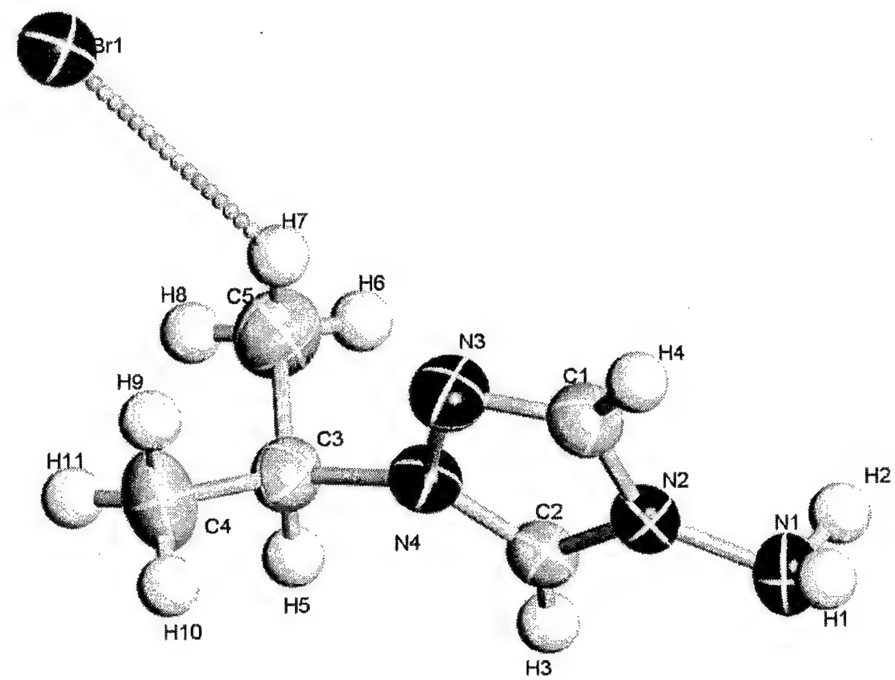
Ionic Liquids



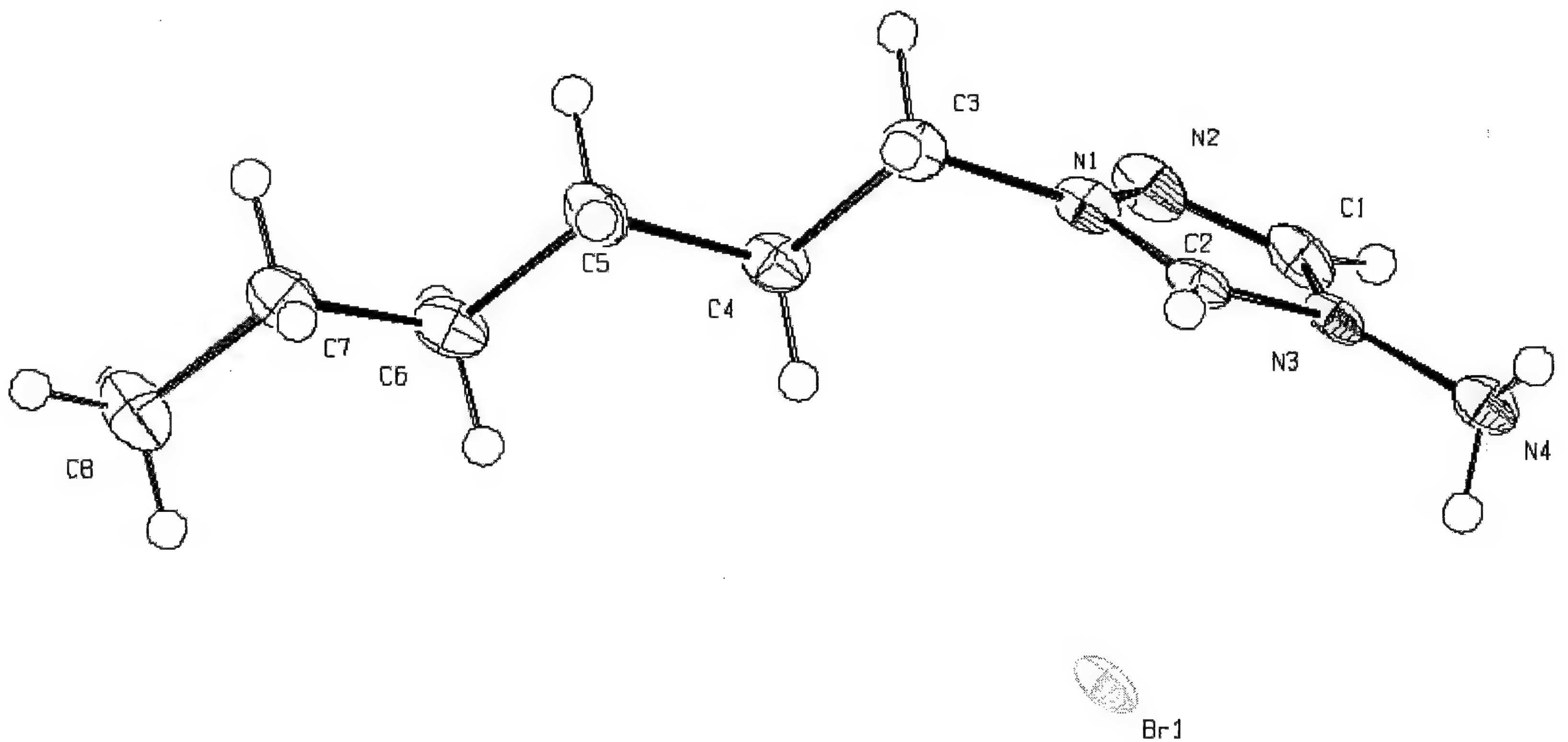
Hydrogen bond contacts in solid 1-n-propyl-4-amino-1,2,4-triazolium bromide

Ionic Liquids



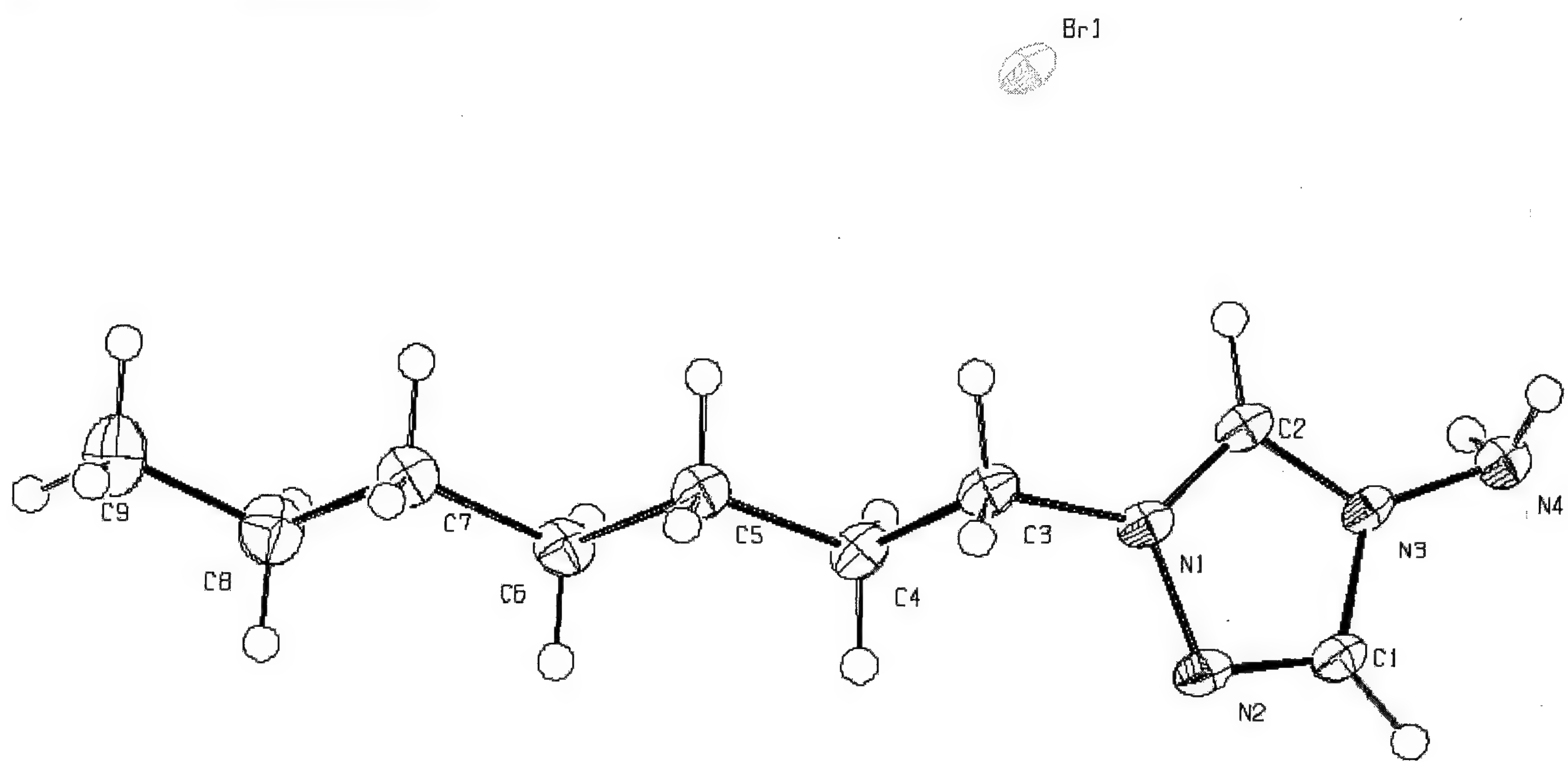
Single crystal x-ray diffraction structure of 1-isopropyl-4-amino-1,2,4-triazolium bromide.

Ionic Liquids



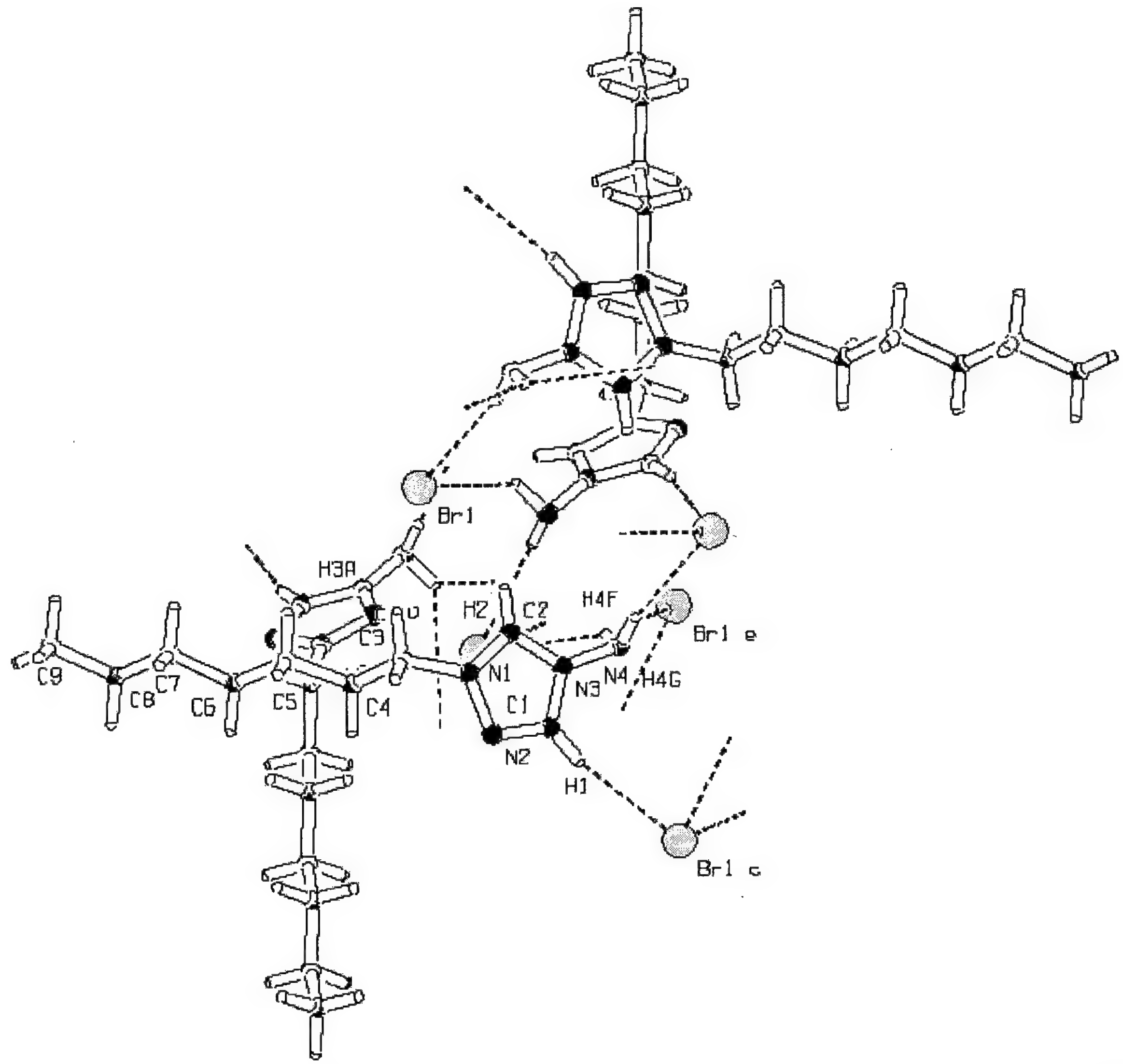
Single crystal x-ray diffraction study of 1-hexyl-4-amino-1,2,4-triazolium bromide.

Ionic Liquids



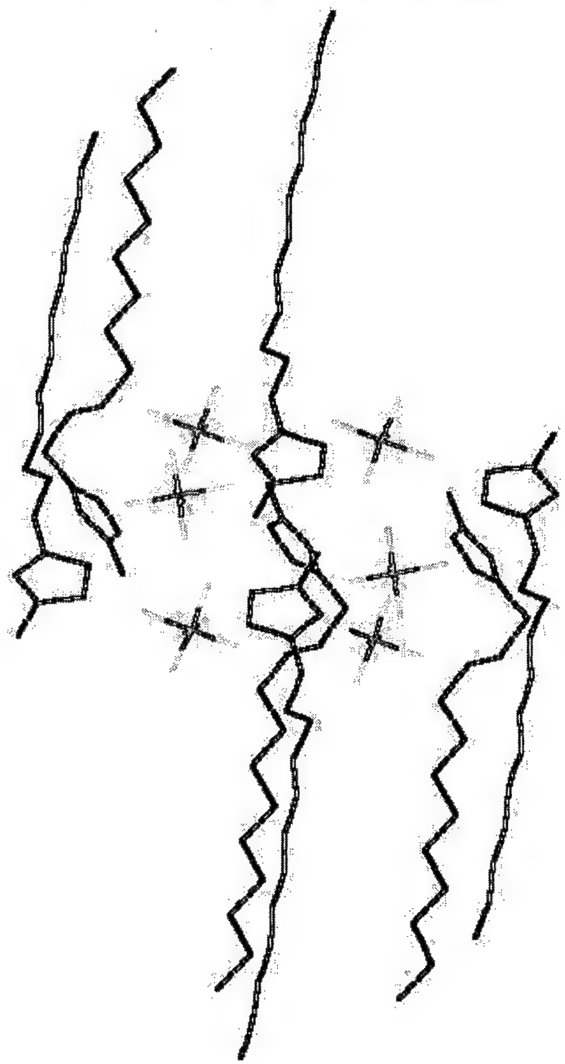
Single crystal x-ray diffraction study of 1-heptyl-4-amino-1,2,4-triazolium bromide.

Ionic Liquids

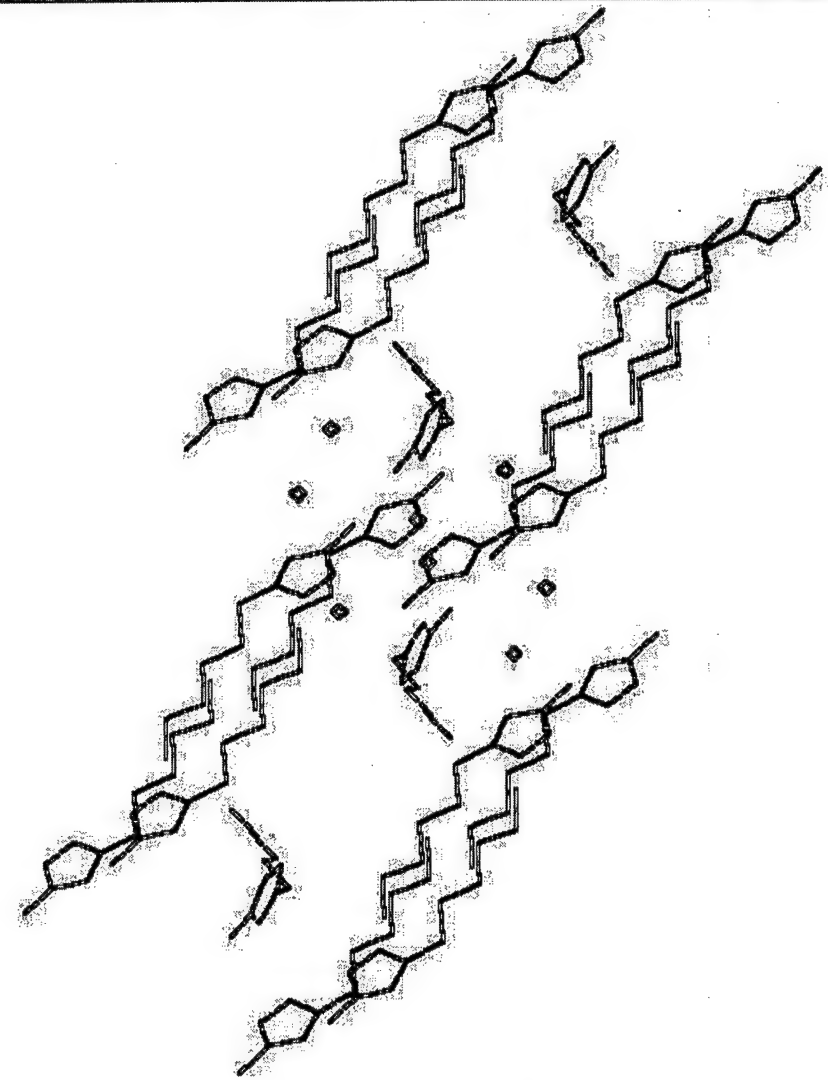


Hydrogen bond contacts in 1-heptyl-4-amino-1,2,4-triazolium bromide

Ionic Liquids



1-dodecyl-3-methylimidazolium hexafluorophosphate*

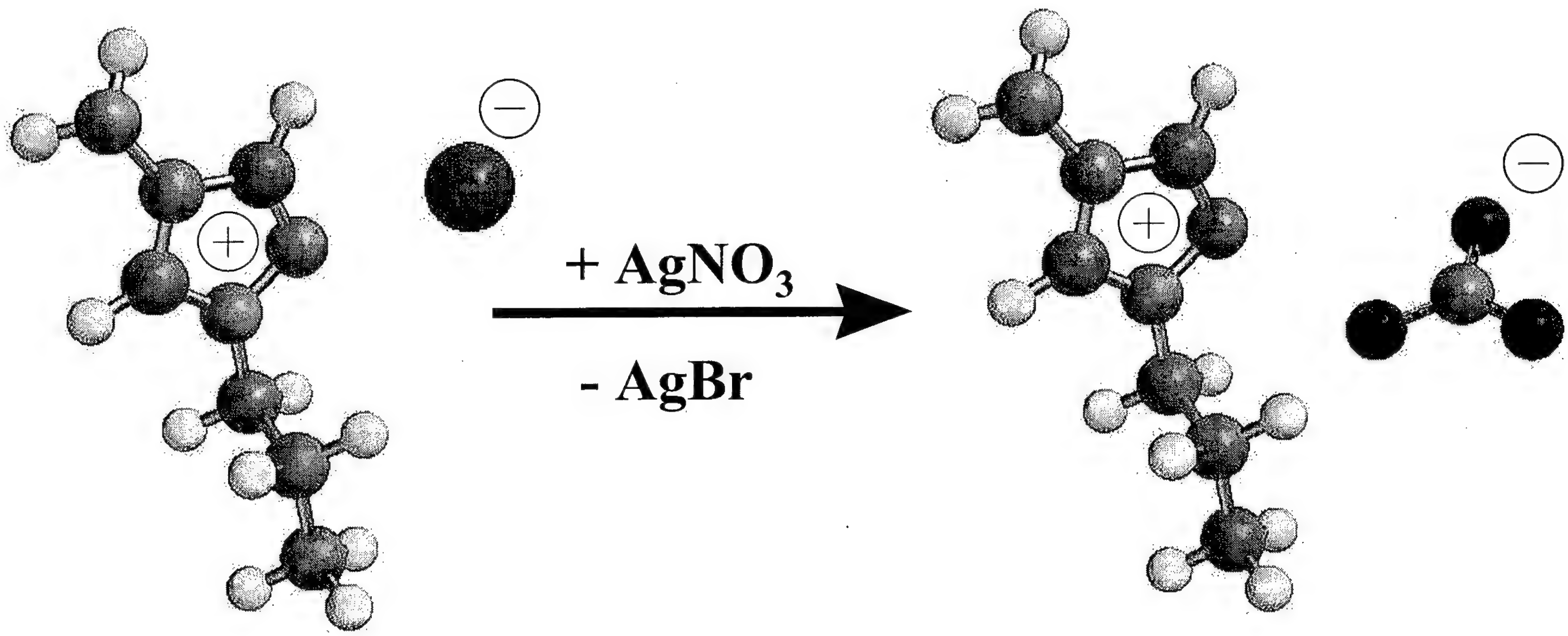


1-hexyl-4-amino-1,2,4-triazolium bromide#

*Gordon, C. M.; Holbrey, J. D.; Kennedy, A. R.; Seddon, K. R. J. Mater. Chem. **1998**, *8*, 2627. #Drake, G. W.; Hawkins, T. W.; Tollison, K.; Hall, L.; Vij, A. **2003** manuscript in progress.

Ionic Liquids

But halides are only the start…
Nitrates were best made through silver nitrate metathesis in methanol.



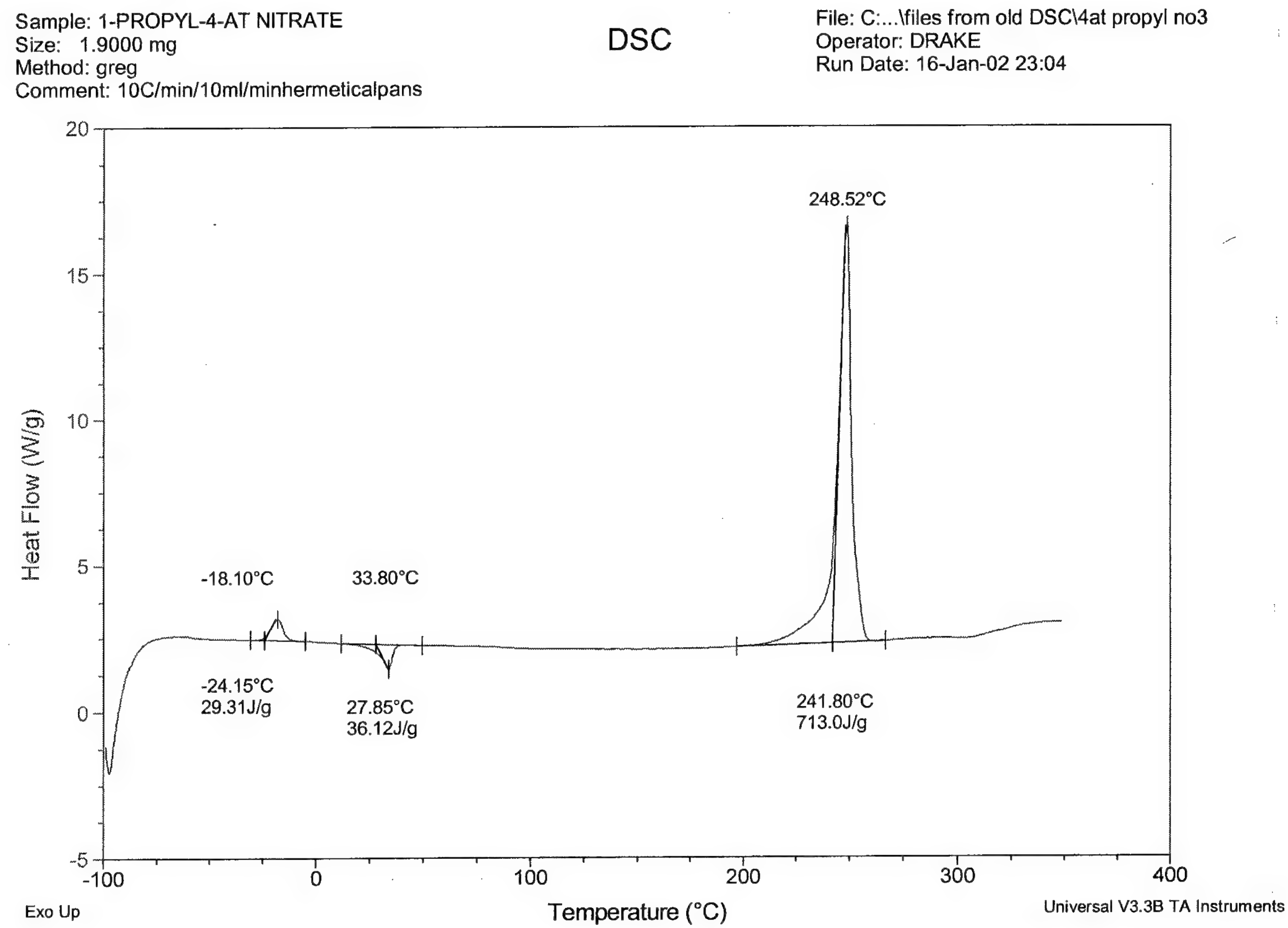
This route led to the best materials as the silver bromide was easily removed.

Ionic Liquids

1-substituted-4-amino-1,2,4-triazolium nitrate salts are more stable.

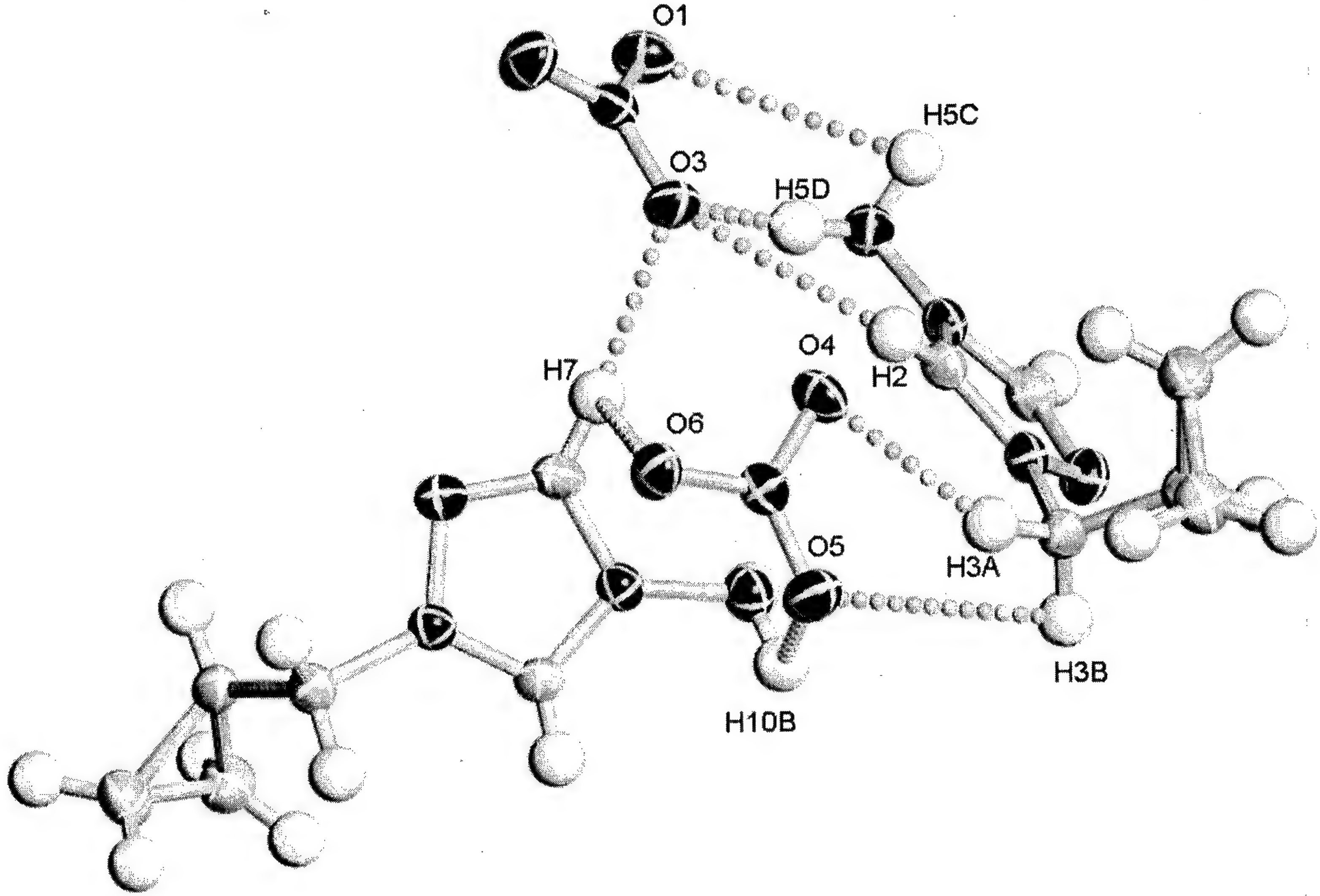
Salt	melting point(°C)	decomp onset(°C)	ρ(g/cm^3, est.)
1-methyl	54	185	1.57
1-ethyl	5	185	1.39 (1.38)
1-n-propyl	34	190	1.35
1-isopropyl	53	175	1.37 (1.43)
1-n-butyl	-25 (g)	190	1.31
1-(2-ethanol)	-50 (g)	180	1.48
1-methylcyclopropyl	56	190	1.36 (1.44)
1-(2-propenyl)	10	165	1.23
1-n-pentyl	26	170	1.29
1-n-hexyl	-2	160	1.26
1-n-heptyl	31	160	1.24
1-n-octyl	29	170	1.22
1-n-nonyl	53	175	1.20
1-n-decyl	49	185	1.18

Ionic Liquids



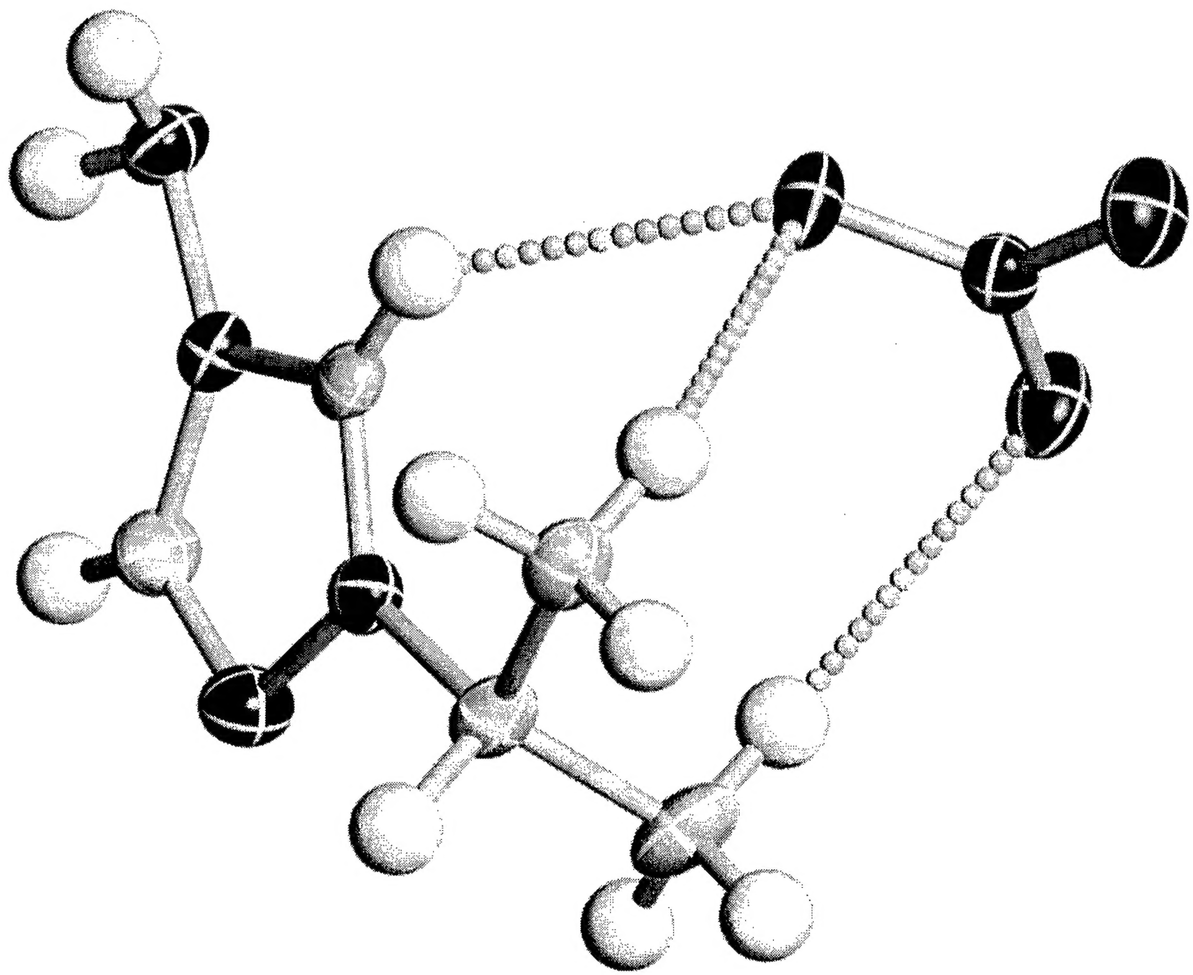
DSC of 1-n-propyl-4-amino-1,2,4-triazolium nitrate

Ionic Liquids



Single crystal x-ray diffraction study of 1-methylcyclopropyl-4-amino-1,2,4-triazolium nitrate.

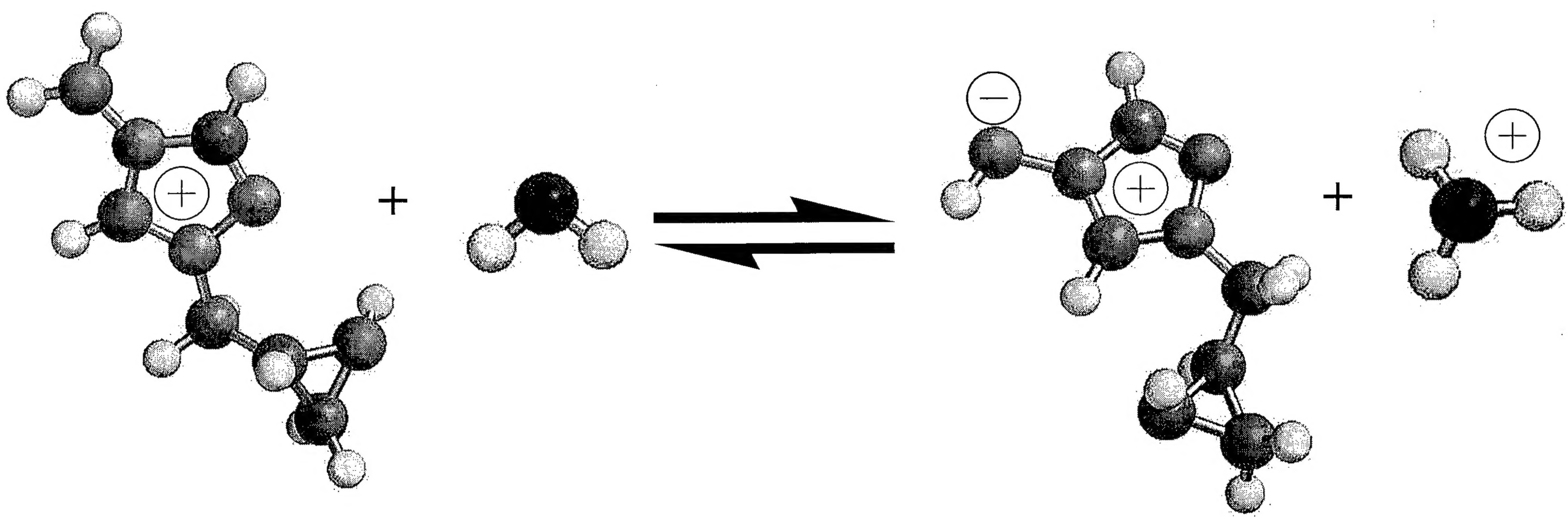
Ionic Liquids



Single crystal x-ray diffraction structure of 1-isopropyl-4-amino-1,2,4-triazolium nitrate

Ionic Liquids

The new energetic cations are weakly acidic in nature, aqueous solutions have a pH of around 4 which suggests the equilibrium involving a zwitterionic 1-alkyl-4-amido-1,2,4-triazolium species. This equilibrium could be one possible way for the ionic liquids to "come apart".



Ionic Liquids

Summary and Conclusions

Oxyamines and nitrocyanamide ions make for low melting and energetic salts, however both are plagued by poor thermal behavior and impact/friction sensitivity.

A large new class of low melting salts which should be considered as new members of the well known class of materials referred to as ionic liquids has been synthesized and well characterized.

Using asymmetric cation shapes and poor cation-anion fit, an analogue system to the well known 1,3-dialkylsubstituted imidazolium cation family, based upon 1-substituted-4-amino-1,2,4-triazolium cations paired with the bromide and nitrate ions has been explored.

Facile synthesis routes from commercially available materials coupled with high yield and purity reactions make these new materials very exciting.

Several single crystal x-ray diffraction studies of several structures have been carried out proving the expected structure as well as revealing extensive hydrogen bonding in the solid state.

Physical properties of 1-substituted-4-amino-1,2,4-triazolium salts included much higher viscosities, higher densities, and much more polar behavior than that of imidazolium ionic liquids.

Ionic Liquids

ACKNOWLEDGEMENTS

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- CLAUDE MERRILL
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